FOOD PRESERVATION SECTION
C.S.I.R.O.

REFLUX IN COUNTER-CURRENT DISTRIBUTION

I. THE ACID-BASE PROCESS

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Summary

A method for separating weak acids or bases is described based on counter-current distribution between an organic solvent and an aqueous phase containing their salts. The process is carried out in a Craig tube system modified to permit solvent flow in both directions. By means of stripping sections the system is run under total or partial reflux. This process is closely analogous to fractional distillation, each tube being equivalent to two theoretical plates. The separation attainable in such a system at equilibrium and the rate of approach to equilibrium are discussed quantitatively and optimum operating conditions evaluated. As an example the separation of *o*- and *p*-toluic acids is described.

I. Introduction

The components in a mixture of weak acids or bases can be separated by a solvent extraction process in which advantage is taken of their different dissociation constants as well as their different partition coefficients. When an organic liquid phase containing the undissociated acids or bases is mixed with an aqueous solution of their alkali or mineral acid salts, the organic phase becomes enriched with the weaker electrolytes. If the two solvent streams are flowing in opposite directions through a contacting device, progressive enrichment occurs. If, further, provision is made at both ends for total or partial exchange of solute between the solvent phases, by the addition of mineral acid or alkali, the system is analogous to a fractional distillation column operating under total or partial reflux. The separation of the penicillin acids from a crude extract by this method has been described (Minty *et al.* 1953). The technique has also been applied to the separation of the alkaloids, heliotrine and lasiocarpine (Weiss 1955).

In Weiss' work fractionation was effected in a pulsed packed column through which the solvents were in continuous flow. It is the purpose of this paper to show that the number of theoretical stages conveniently attainable‡ can be greatly increased by forming the fractionating section of elements that can be isolated from one another and by making solvent flow intermittent. The process may be carried out in a modified Craig apparatus in which, after suitable loading, separation is effected by repetition of the following sequence of operations—equilibration–lower phase transfer–equilibration–upper phase transfer. One such sequence will be termed a "double transfer".

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‡ Mr. D. E. Weiss (personal communication) estimates the H.E.T.P. of his column to have been 2 ft.

II. Method

Modifications to the tube system of the Craig counter-current distribution machine permit movement of both solvent phases in opposite directions (Verzele and Alderweireldt 1954; von Metzsch 1959; Wilhelm and Foos 1959). Thus modified, the tube system is essentially a set of intermittently operated mixer–settler units, in which upper and lower phases are transferred alternately rather than simultaneously. The design of the tubes used in the work described here was that of Verzele, although those of Wilhelm and Foos would appear to be particularly suitable. The method of use is shown diagrammatically in Figure 1, where each double rectangle represents a tube containing an upper and a lower liquid phase. To separate, for instance, a mixture of weak acids, these are dissolved in an organic solvent and the solution extracted $2M$ times with aqueous alkali, M being the number of tubes in the fractionating section. The total alkali used is just sufficient to neutralize the acids and the volume of each extract is equal to the lower-phase capacity of a fractionating tube. The extracts are

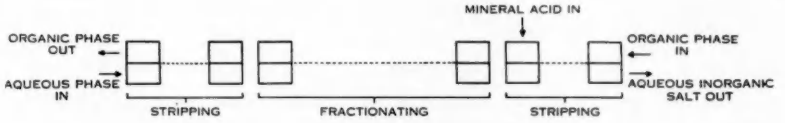

Fig. 1.—Diagrammatic representation of the acid-base reflux process.

loaded successively into the first fractionating tube from which they travel through the system to the first acid-stripping tube. Here mineral acid equivalent to the alkali of an extract is added, followed by organic solvent which abstracts the liberated weak acids from the aqueous phase. The lower-phase capacity of the acid-stripping tubes is sufficient to accommodate the increase in volume. The upper phases containing the liberated acids return to the fractionating section and are passed along it, being equilibrated successively with each of the oncoming aqueous extracts. The exhausted aqueous phases from the first acid-stripping tube are treated with further organic solvent in the remaining tubes of the acid-stripping section before running to waste.

When the organic phase containing the modified first extract returns to the first fractionating tube loading is complete. On subsequent lower-phase transfers aqueous alkali of the appropriate strength and volume enters this tube and strips the organic phase of its acids. Subsequent upper-phase transfers remove the spent organic phases to the alkali-stripping section where they make contact successively with further similar alkali fractions before emerging to waste. The solutes remain contained in the tube system, their distribution tending to a steady state as refluxing proceeds.

The method of operation has been described assuming the organic solvent to be less dense than water. The process works equally well if the organic phase is denser than water.

III. Theory

(a) *General*

We consider a mixture of organic acids HA_1, HA_2, etc. distributed between an organic solvent and aqueous alkali, which we will assume for definiteness to be sodium hydroxide. If $[HA_n]$ is the concentration of acid HA_n in the organic phase, $[HA'_n]$ the concentration of undissociated HA_n in the aqueous phase, and $[A_n^-]$ the concentration of the ions A_n^- in the aqueous phase, then the following equilibrium relations must hold :

$$[HA'_n]=\frac{1}{P_n}[HA_n], \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$[H^+][A_n^-]=K_n[HA'_n], \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$[H^+]+[Na^+]=[OH^-]+\Sigma_n[A_n^-]. \quad \ldots\ldots\ldots\ldots \quad (3)$$

Here P_n is the partition constant for distribution of undissociated HA_n between the two phases and K_n is the dissociation constant of HA_n. The third equation expresses the condition of electrical neutrality of the aqueous phase. It has been assumed that the salts NaA_n are completely dissociated in the aqueous phase and not present in the organic phase. Substituting from (1) and (2) in (3) we find that the hydrogen ion concentration is determined by the equation

$$[H^+]([H^+]+[Na^+])=K_w+\Sigma_n\frac{K_n}{P_n}[HA_n], \quad \ldots\ldots\ldots \quad (4)$$

where K_w is the dissociation constant of water.

In practice, the hydrogen ion concentration is very much smaller than $[Na^+]$ so that (4) becomes

$$[H^+]=\frac{1}{[Na^+]}\left(K_w+\Sigma_n\frac{K_n}{P_n}[HA_n]\right). \quad \ldots\ldots\ldots\ldots \quad (5)$$

On solving (4) as a quadratic in $[H^+]$ we see that the condition that (5) should be valid is

$$K_w=\Sigma_n\frac{K_n}{P_n}[HA_n]\ll\tfrac{1}{4}[Na^+]^2. \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

If this condition is satisfied, $[HA''_n]$, the total concentration of HA_n in the aqueous phase, is given by

$$\frac{[HA''_n]}{[HA_n]}=\frac{[HA'_n]+[A_n^-]}{[HA_n]}$$

$$=\frac{1}{P_n}+\frac{K_n}{P_n}[Na^+]\Big/\left(K_w+\Sigma_m\frac{K_m}{P_m}[HA_m]\right), \quad \ldots\ldots\ldots \quad (7)$$

where the summation over m includes HA_n as well as the other solutes. Equation (7) gives the distribution of the acids between the phases for the general case of a multicomponent mixture of acids.

If distribution of the undissociated acids strongly favours the organic phase, so that the partition constants P_n are large, it is a good approximation to neglect

the term $1/P_n$ in (7). If, in addition, the acids are not too weak (if K_n/P_n is not less than about 10^{-13}) then K_w may also be neglected. In these circumstances it is easily seen from (7) that the total amount of acid in the aqueous phase is equal to the amount of sodium ion. If, also, we arrange initially that the total amount of acid in each organic phase is the same as that in each aqueous phase, then this situation will persist throughout. Under these conditions (7) may be written in the form

$$x_n = \frac{K_n}{P_n} y_n \Big/ \left(\sum_m \frac{K_m}{P_m} y_m \right), \quad \ldots\ldots\ldots\ldots\ldots \quad (8)$$

where x_n is the concentration of HA_n in the aqueous phase expressed as mole fraction of total acid and y_n is the corresponding quantity for the organic phase. Equation (8) is identical with the equations used in distillation problems involving multicomponent mixtures. Using (8) the separation process can be followed theoretically through all stages.

During the initial extraction of the acids with successive unit quantities of alkali, equation (8) takes the form

$$x_n = \frac{K_n}{P_n}(Q_n - x_n) \Big/ \left[\sum_m \frac{K_m}{P_m}(Q_m - x_m) \right], \quad \ldots\ldots\ldots\ldots \quad (9)$$

where Q_n are the amounts of acids present before the extraction, in units of the amount required to neutralize unit quantity of alkali. These equations can be solved for the x_n which are then subtracted from the Q_n to give the Q_n for the next extraction.

When the first extract has passed through the fractionating section, it is acidified and its acids returned in a counter-current organic phase. In subsequent operations this organic phase is equilibrated with each of the following extracts. In each equilibration the acids present are competing for half the amount of alkali required to neutralize them. The new distribution is again given by (9) with Q_n now equal to the total amount of HA_n in the tube concerned. In the same way (9) is applied to determine the new distribution at each stage of the refluxing process.

(*b*) *Equilibrium*

As refluxing proceeds the solute distribution throughout the tube system tends to a steady state. If the organic phase of the first tube, the aqueous phase of the first tube, the organic phase of the second tube . . . are numbered 1, 2, 3, . . . , and if $x_{n,\lambda}$ represents the concentration of HA_n in phase λ, then the equilibrium concentrations are determined by the equations

$$x_{n,\lambda+1} = \frac{K_n}{P_n} x_{n,\lambda} \Big/ \left(\sum_m \frac{K_m}{P_m} x_{m,\lambda} \right). \quad \ldots\ldots\ldots\ldots \quad (10)$$

When λ is odd, equation (10) is always valid, since it gives the acid composition of the aqueous phase in equilibrium with an organic phase (cf. eqn. (8)). However, *at equilibrium* it also holds when λ is even. Thus at equilibrium the compositions of any two successive phases are related by (10). Table 1 shows

that, if the compositions of all phases satisfy this relation, then the system is indeed in a steady state since the double transfer operation leaves the phase compositions unchanged. The essential point is that, in the steady state, the equilibration following an upper- or lower-phase transfer simply interchanges the acid compositions of the two phases in each tube.

TABLE 1

Operation	Phase	Phase Compositions					
Original state	Organic	1	3	5	7	9	—
	Aqueous	2	4	6	8	10	—
Lower - phase transfer	Organic	1	3	5	7	9	—
	Aqueous	—	2	4	6	8	10
Equilibration	Organic	—	2	4	6	8	10
	Aqueous	1	3	5	7	9	—
Upper - phase transfer	Organic	2	4	6	8	10	—
	Aqueous	1	3	5	7	9	—
Equilibration	Organic	1	3	5	7	9	—
	Aqueous	2	4	6	8	10	—

Equation (**10**) thus provides a method for calculating the equilibrium distribution for a multicomponent system. For a binary mixture, equation (**8**) may be written in the simpler form

$$\frac{y_1}{1-y_1}=\alpha\frac{x_1}{1-x_1}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{11})$$

where x_1 and y_1 are the concentrations of HA_1, those of HA_2 being $(1-x_1)$ and $(1-y_1)$. Equation (**11**) is the Fenske equation of distillation theory (Rose 1951). The constant α, which is exactly analogous to the relative volatility, is given by

$$\alpha=\frac{K_2P_1}{K_1P_2}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{12})$$

as has already been shown by Twigg (1949), Walker (1950), Minty *et al.* (1953), and Weiss (1955). Thus in favourable cases the partition effect increases the separation over that obtained by virtue of differing acid strengths, while in other cases the reverse is true. For a binary mixture equations (**10**) may be solved in simple form

$$\frac{x_{1,\lambda}}{1-x_{1,\lambda}}=c\alpha^{\lambda}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{13})$$

where the constant c depends on the total amounts of the two acids present in all the tubes. Equation (**13**) shows that the number of theoretical plates, in distillation terminology, is $2M-1$ when the fractionating section contains M tubes. This somewhat surprising result is a consequence of the fact that the

TABLE 2

Operation	Phase	Phase Composition						
Original state	Organic	—	1	2	3	4	5	6
	Aqueous	1	2	3	4	5	6	—
Simultaneous two-phase transfer	Organic	1	2	3	4	5	6	—
	Aqueous	—	1	2	3	4	5	6
Equilibration	Organic	—	1	2	3	4	5	6
	Aqueous	1	2	3	4	5	6	—

solvents are transferred alternately, each transfer being followed by an equilibration. If the solvents were transferred simultaneously, as in a conventional intermittently operated mixer–settler system, the number of theoretical stages would be M. This is illustrated by Table 2, which shows schematically that the equilibrium state in such a system is reached when the solute composition of the lower phase in one element is *the same* as that of the upper phase in the next.

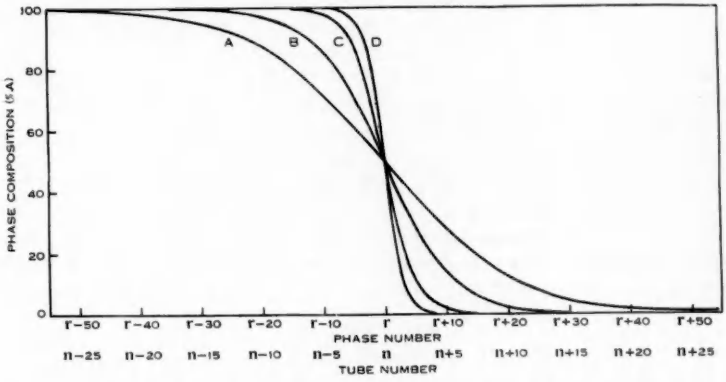

Fig. 2.—Solute distribution at equilibrium for equal amounts of two components. For A, B, C, and D the values of α are 1·1, 1·2, 1·5, and 2·0.

For equal amounts of the two acids in an M tube system, equation (**13**) becomes

$$\frac{x_{1,\lambda}}{1-x_{1,\lambda}} = \alpha^{(\lambda - M - \frac{1}{2})}. \qquad \text{..... (14)}$$

Some representative equilibrium curves calculated from (**14**) are shown in Figure 2.

Figures 3 (*a*) and 3 (*b*) show the equilibrium distribution for a ternary mixture calculated from equations (**10**). In this example the relative values

K_n/P_n are 1, 2, and 4 for the components HA_1, HA_2, and HA_3. The total amount of HA_2 present is 3·41 units, which value arose from the concentrations of the three acids in phase 1 arbitrarily chosen to start the calculations. To calculate for a system containing a known amount of intermediate acid (or acids) it is necessary to determine the concentrations in phase 1 by trial and error.

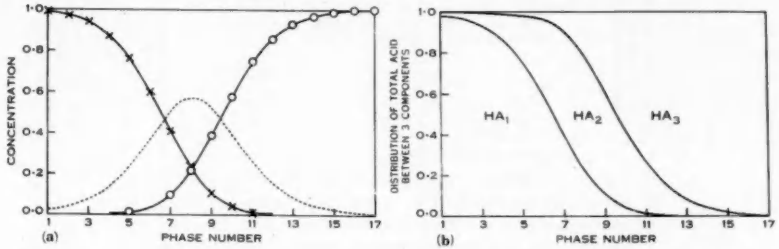

Fig. 3.—(*a*) Equilibrium concentrations after separation of a ternary mixture, HA_1, HA_2, HA_3 whose K/P values are 1, 2, and 4 respectively. ×—×HA_1, . . . HA_2, ○—○ HA_3. (*b*) The equilibrium distribution of the same ternary mixture.

(*c*) *Approach to Equilibrium*

While Figures 2 and 3 show the results that can be obtained at equilibrium it is important to know how long the approach to equilibrium takes and how far it is economical to proceed. The process can be followed by successive solutions of equations (9) which become simple quadratics for a binary mixture. Some

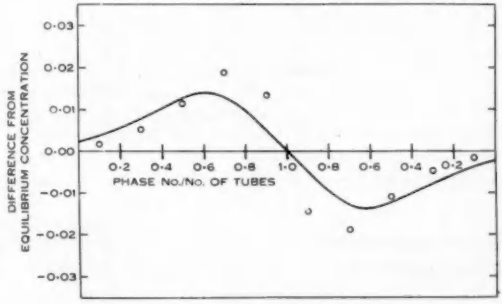

Fig. 4.—Differences from equilibrium concentrations for 10 tube system with $\alpha = 2 \cdot 0$. Circles are directly calculated for loading process +25 double transfers; solid line from equation (**A22**) for uniform loading with 5+25=30 double transfers.

numerical calculations of this kind have been carried through on an IBM 650 electronic computer, and some typical results are shown in Figures 4, 5, and 6. In Appendix I we derive an approximate formula which describes the main features of the approach to equilibrium for a binary system with equivalent amounts of the two acids present.

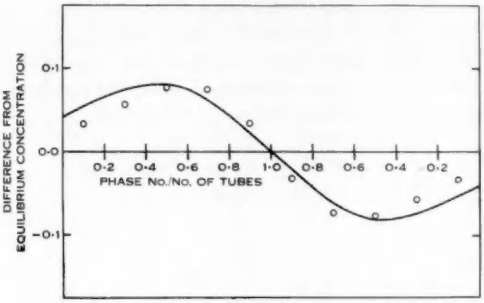

Fig. 5.—Differences from equilibrium concentrations for 10 tube system with $\alpha = 1 \cdot 5$. Circles are directly calculated for loading process + 25 double transfers; solid line from equation (A22) for uniform loading with 5 + 25 = 30 double transfers.

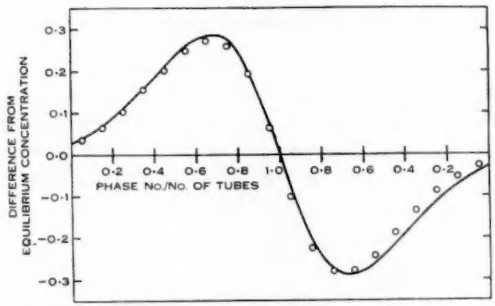

Fig. 6.—Differences from equilibrium concentrations for 20 tube system with $\alpha = 1 \cdot 5$. Circles are directly calculated for loading process + 25 double transfers; solid line from equation (A22) for uniform loading with 10 + 25 = 35 double transfers.

According to this approximation the number of double transfers, N, required to reduce the mole fraction of acid 1 to the value m in phase λ of an M tube system is given by

$$N = \frac{2(\alpha^2+1)}{(\alpha-1)^2} F(\beta, w, m), \quad \ldots\ldots\ldots\ldots \quad (15)$$

where

$$\beta = \tfrac{1}{2} M \frac{\alpha^2-1}{\alpha^2+1}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

$$w = \frac{\lambda}{M}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (17)$$

and the function $F(\beta, w, m)$ is given explicitly in Appendix I. In Figure 7 $F(\beta, w, m)$ is plotted for $m = 0 \cdot 01$ and several values of w; for given α the number of double transfers is directly proportional to $F(\beta, w, m)$ and w is the fractional

yield of material of purity $1-m$ (see Appendix I), while β is proportional to the number of tubes. For a given yield there is a number of tubes requiring a least number of double transfers and this number of tubes is slightly larger than the number of tubes giving the same yield at equilibrium. However, according

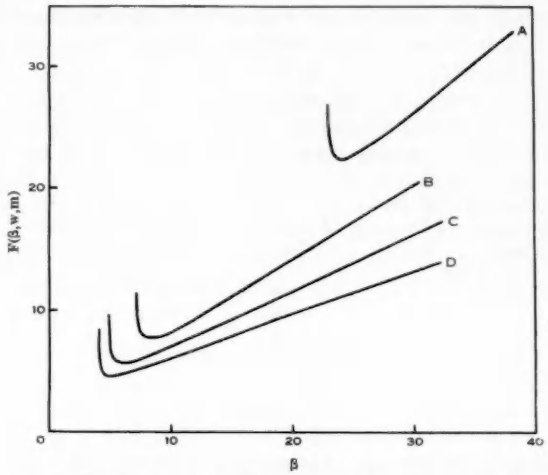

Fig. 7.—The function $F(\beta, w, m)$ for $m=0\cdot01$ and several values of x. A, $x=0\cdot900$; B, $x=0\cdot680$; C, $x=0\cdot536$; D, $x=0\cdot435$.

to these results, a high yield is more economically obtained in two stages, the fractions which are insufficiently pure after the first processing being diluted and reprocessed. This requires fewer tubes and fewer double transfers than would be needed to obtain the same yield in one run. This is shown in Table 3. The

TABLE 3

Yield per Operation	Optimum β	Optimum $F(\beta, w, m)$	No. of Operations for 90% Yield	No. of Operations $\times F(\beta, w, m)$
0·900	24·0	22·5	1	22·5
0·680	8·5	7·7	2	15·4
0·536	6·0	5·6	3	16·8
0·435	5·0	4·6	4	18·4

figures in the first column give the fractional yield of pure material per operation, while the total number of double transfers for 90 per cent. yield is proportional to the numbers in the last column. Thus for 90 per cent. yield one requires fewer double transfers and also fewer tubes if two operations are performed. On the other hand, a 68 per cent. yield is best obtained in one operation, since

the optimum number of double transfers for $w=0\cdot435$ is more than twice the number for $w=0\cdot68$.

Using these results we can calculate the best number of tubes to use for a given separation and the number of double transfers required. It must be remembered, however, that these conclusions are based on an approximation which Figures 4, 5, and 6 show to be most accurate when the number of tubes is large and α is close to one. Some results for several values of α are given in Table 4.

TABLE 4

α	68% Yield—1 Operation		90% Yield—2 Operations		90% Yield—1 Operation	
	Best Number of Tubes	Number of Double Transfers	Best Number of Tubes	Number of Double Transfers	Best Number of Tubes	Number of Double Transfers
1·2	94	940	94	1880	266	2745
1·5	44	200	44	400	125	585
2·0	28	77	28	154	80	225
3·0	21	39	21	78	60	113

(*d*) *Partitioning Effect and Stripping Section*

At each double transfer some undissociated acid remains in the "stripped" aqueous phase. If the term $1/P_n$ in equation (**7**) is neglected, this effect is left out of account. To estimate how many stripping tubes are required to make loss of solute negligible, calculations were made including this term but assuming that all the partition constants had the same value, P. These showed that the distribution of total acid in the tubes rapidly approached a steady state, which can be derived by simple algebra. If T_n is the total acid in tube n (where the fractionating section has $n=1, 2, \ldots, M$ and the stripping section $n=M+1$, $M+2, \ldots, M+k$) then in the steady state

$$T_1=\frac{p}{p-q}-\gamma\frac{p^2}{q}, \qquad \ldots\ldots (18)$$

$$T_n=\frac{2p}{p-q}-\gamma\left(\frac{q}{p}\right)^{2(n-2)} \qquad 2\leqslant n\leqslant M, \qquad \ldots\ldots (19)$$

$$T_n=\frac{q}{p(p-q)}\left(\frac{q}{p}\right)^{2(n-M-1)} \qquad M+1\leqslant n\leqslant M+k, \qquad \ldots\ldots (20)$$

where

$$p=\frac{P}{P+1}, \qquad \ldots\ldots (21)$$

$$q=\frac{1}{P+1}. \qquad \ldots\ldots (22)$$

The constant γ depends on the total amount of acid present and is less than $q/p(p-q)$ since otherwise the first tube contains no acid and the number of effective fractionating tubes is reduced by one. Thus each tube, except the

first few in which there is a slight deficiency, contains nearly $p/(p-q)$ units of acid in each phase. The amount of acid passing out of the stripping section at each double transfer is T_{M+k} or $p(q/p)^{2k}/(p-q)$. After a quantity of solute $2p/(p-q)$ is lost in this way the number of effective fractionating tubes falls by one. The number of double transfers required to produce this loss is $2(p/q)^{2k}$ or $2P^{2k}$ (note that k is the number of stripping tubes). It is apparent that the loss per double transfer can be made negligibly small.

In using equations (**11**) and (**12**) we assumed that each phase in the fractionating section contained one unit of total acid (where one unit of alkali is used in each initial extract) whereas the above argument shows that most phases contain $p/(p-q)$ or $P/(P-1)$ units of acid. It can be verified from (**1**)-(**6**) that the effect of this slight excess of acid on the relative distribution of the different acids is negligible for all likely values of K_n ($10^{-2} > K_n > 10^{-12}$) and for $P_n > 10$. For values of P_n between 10 and 2, in order to make theoretical predictions it would be necessary to use (**7**) rather than the approximate equations (**9**). Systems in which P_n is less than about 2 are unlikely to be appropriate for the present process.

IV. Experimental

A mixture of equal parts of *o*-toluic acid ($K = 12{\cdot}3 \times 10^{-5}$) and *p*-toluic acid ($K = 4{\cdot}24 \times 10^{-5}$) was chosen as suitable to test the process as described. The separation factor, α, was determined by two methods.

(i) *o*-Toluic acid (2·058 g) was shaken with a mixture of ether-saturated 0·189N NaOH (40 ml) and moist ether (40 ml). After separation, the ether layer was shaken with excess 0·100N NaOH, which was then back titrated with 0·100N HCl. Undissociated acid in the original aqueous layer was measured by titration to the phenolphthalein end point with 0·100N NaOH

$$P\ (ortho) = \frac{\text{undissociated acid in ether layer}}{\text{undissociated acid in aqueous layer}} = 104.$$

Similarly estimated

$$P\ (para) = 83.$$

And from (**12**)

$$\alpha = \frac{83 \times 12{\cdot}3}{104 \times 4{\cdot}24} = 2{\cdot}3.$$

(ii) *o*-Toluic acid (1·029 g) and *p*-toluic acid (1·029 g) were dissolved in ether (40 ml) and shaken for 4 min with 0·189N NaOH (40 ml). After isolation, the composition of the acid mixture in each layer was estimated from the m.p. as described below. From (**11**)

$$\alpha = \frac{o\text{-toluic (aq.)} \times p\text{-toluic (org.)}}{o\text{-toluic (org.)} \times p\text{-toluic (aq.)}}$$

whence

$$\alpha = 2{\cdot}25(\pm 0{\cdot}025).$$

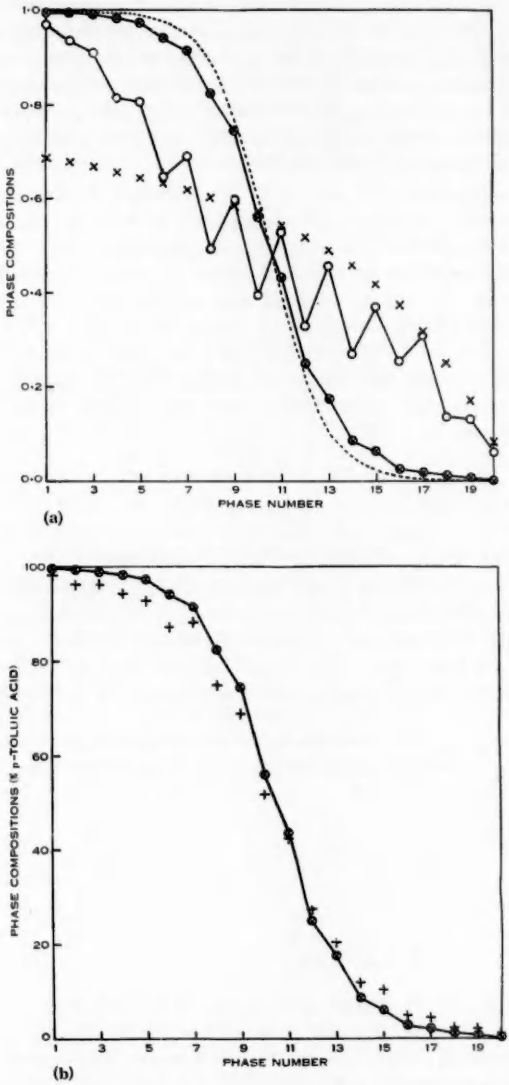

Fig. 8.—(*a*) The separation of two components with $\alpha=2\cdot3$ in 10 fractionating tubes. ×—× composition of initial extracts, ○—○ phase composition after loading, ⊗—⊗ phase composition after 15 double transfers, ···· phase composition at equilibrium. (*b*) The separation of *o*- and *p*-toluic acids in 10 fractionating tubes. ⊗—⊗ phase composition after 15 double transfers calculated for $\alpha=2\cdot3$. ++ phase composition, experimental.

o-Toluic acid (9·906 g) and *p*-toluic acid (9·906 g) were dissolved in water-saturated ether (770 ml) and the solution extracted 20 times with 38·5 ml portions of ether-saturated 0·189N NaOH. The apparatus, into which the extracts were loaded as described in Section II, consisted of a bank of 20 Verzele tubes, mounted for automatic shaking, of which tubes 1–5 were the alkali-stripping section, tubes 6–15 the fractionating section, and tubes 16–20 the acid-stripping section. The bottom phase capacity in each of tubes 1–15 was adjusted to 38·5 ml by the insertion of polythene-tipped glass rod; that in tubes 16–20 was 40 ml. Acidifications at tube 16 were effected by the addition of 1·5 ml portions of 5N HCl. Two hundred and fifty to three hundred agitations (4–5 min shaking time) were performed at each equilibration.

When loading was complete, refluxing was continued through 15 double transfers, then the solute in each of the 20 phases in the fractionating tubes was isolated and the m.p. determined. The composition of the fractions was estimated from the m.p.-composition diagram for *o*- and *p*-toluic acids constructed from the data of Lettré *et al.* (1937). Calculated phase compositions at four stages are shown in Figure 8 (*a*) and the experimental results in Figure 8 (*b*).

V. Discussion

We have shown that an M-tube fractionating section contains $2M-1$ theoretical stages equivalent to the theoretical plates of distillation theory. The number of plates usually attained in distillation is not greater than about 100. Since a Craig machine of 1000 tubes has been constructed, it would appear that the potential of the present process is considerable.

The theoretical discussion has been concerned mainly with mixtures of two solutes in equivalent amounts. In other cases, for instance where an acid to be processed contains a minor amount of an impurity acid, the equilibrium curve (Fig. 2) is not altered in shape. The final distribution is found by moving the curve laterally until the proportions of the two components are appropriate.

The situation exemplified by Figures 3 (*a*) and 3 (*b*) merits brief discussion. Separation of HA_1 from HA_2 and HA_3 is sharper than would occur between HA_1 and HA_2 alone, but the minor component, HA_2, could only be obtained pure by running the process at higher dilution in a greater number of tubes or by reprocessing the centre fractions. In either case the distribution would be as for binary systems containing HA_1 and HA_2 or HA_2 and HA_3. However, the overlap between HA_1 and HA_3 in Figures 3 (*a*) and 3 (*b*) is less than that of a binary mixture of these acids, so that the presence of HA_2 would be advantageous if this acid could be removed by other means after separation of the two major components.

Partial reflux may be obtained with the present tube system by making the strength of the fixed volume mineral acid additions insufficient to liberate all the organic acids of an aqueous phase. A part of the solutes of such a phase would then flow out of the system instead of being returned. To retain the same number of fractionating stages the strength of the entering alkali phases would be correspondingly reduced. Alternatively, as was used by Weiss, a reservoir of mixed solutes could be incorporated, making the process closely analogous to

batch fractional distillation in practice as well as in theory. Tube capacity and the number of tubes could then be reduced although processing would take longer. With a reservoir, the process could also be operated in a manner analogous to continuous fractional distillation.

VI. Acknowledgments

We thank Dr. A. C. Hurley, Dr. V. W. Maslen, and Mr. I. Brown for valuable discussion, and Miss Adrienne Petty and Mr. J. A. Dods for skilled technical assistance.

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Appendix I

The Approach to Equilibrium

In a binary mixture the mole fractions x_n, y_n of HA_1 in organic and aqueous phases of the tube n are changed by a lower-phase transfer to x'_n, y'_n and by the subsequent upper-phase transfer to x''_n, y''_n, according to the equations

$$\frac{y_n}{1-y_n}=\frac{\alpha x_n}{1-x_n}, \quad \text{(A1)}$$

$$\frac{y'_n}{1-y'_n}=\frac{\alpha x'_n}{1-x'_n}, \quad \text{(A2)}$$

$$x'_n+y'_n=x_n+y_{n-1}, \quad \text{(A3)}$$

$$\frac{y''_n}{1-y''_n}=\frac{\alpha x''_n}{1-x''_n}, \quad \text{(A4)}$$

$$x''_n+y''_n=x'_{n+1}+y'_n. \quad \text{(A5)}$$

We introduce the variables $u_n=(1-x_n)/x_n$ and $v_n=(1-y_n)/y_n$ and replace (A3), (A5) by the approximations

$$u'_n+v'_n=u_n+v_{n-1}, \quad \text{(A6)}$$

$$u''_n+v''_n=u_{n+1}+v_n. \quad \text{(A7)}$$

These are good approximations to (A3), (A5) when x_n, y_n are close to 1; if α is not too far from 1, so that the change of concentration from one phase

to the next is always small, they are good approximations for all values of x_n, y_n between $\frac{1}{2}$ and 1. Since u_n is equal to αv_n etc., we find, using (A6) and (A7), that

$$u_n'-u_n=(s^2u_{n+1}-r^2u_n)-(s^2u_n-r^2u_{n-1}), \quad \ldots\ldots \text{(A8)}$$

where

$$r=1-s=\frac{\alpha}{\alpha+1}. \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(A9)}$$

Equations like (A8) can be derived more rigorously for the differences of the concentrations from the equilibrium values if it is assumed that these differences are already small, so that the system is close to equilibrium. However, (A8) should be approximately valid even if the system is not close to equilibrium.

We replace (A8) by a partial differential equation:

$$\frac{\partial u}{\partial N}=\frac{\partial}{\partial n}\left[\tfrac{1}{2}(r^2+s^2)\frac{\partial u}{\partial n}-(r^2-s^2)u\right]$$

$$=\tfrac{1}{2}\frac{(\alpha^2+1)}{(\alpha+1)^2}\frac{\partial}{\partial n}\left(\frac{\partial u}{\partial n}-\frac{2(\alpha^2-1)}{\alpha^2+1}u\right), \quad \ldots\ldots \text{(A10)}$$

where N is the number of double transfers, n the tube number. This is a heat conduction equation with a convection term; the solutes are carried along by the solvents and at the same time spread out from tube to tube. The steady state solution of (A10) is

$$u=A\exp\left[2(\alpha^2-1)n/(\alpha^2+1)\right], \quad \ldots\ldots\ldots \text{(A11)}$$

where A is a constant. The correct equilibrium distribution derived directly from (A1)–(A5) or from (A8) is

$$u=A\exp\left(2n\ln\alpha\right). \quad \ldots\ldots\ldots\ldots\ldots \text{(A12)}$$

The difference between (A11) and (A12) is a measure of the approximation involved in replacing (A8) by (A10); when α is close to 1, $(\alpha^2-1)/(\alpha^2+1)$ and $\ln\alpha$ are not very different.

We introduce the variables

$$t=\frac{2}{M^2}\frac{(\alpha^2+1)}{(\alpha+1)^2}N, \quad \ldots\ldots\ldots\ldots \text{(A13)}$$

$$w=\frac{2n-1}{M}=\frac{\lambda}{M}, \quad \ldots\ldots\ldots\ldots \text{(A14)}$$

$$\beta=\tfrac{1}{2}M\frac{\alpha^2-1}{\alpha^2+1}, \quad \ldots\ldots\ldots\ldots\ldots \text{(A15)}$$

where M is the number of tubes, n the tube number, and λ the phase number. Then (A8) becomes

$$\frac{\partial u}{\partial t}=\frac{\partial^2 u}{\partial w^2}-2\beta\frac{\partial u}{\partial w} \qquad 0<w<1,\ t>0. \quad \ldots\ldots \text{(A16)}$$

We also introduce the boundary and initial conditions

$$\frac{\partial u}{\partial w}-2\beta u=0 \qquad w=0,\ t>0, \quad \ldots\ldots\ldots\ldots \textbf{(A17)}$$

$$u=1 \qquad w=1,\ t>0, \quad \ldots\ldots\ldots\ldots \textbf{(A18)}$$

$$u=1 \qquad 0<w<1,\ t=0, \quad \ldots\ldots\ldots \textbf{(A19)}$$

expressing that there is no flow of solute out of the end of the system and that the concentrations of the two acids remain equal at the centre of the system and are initially equal throughout. The latter condition of uniform loading differs from the loading process described in the text; we can make approximate allowance for the difference by assuming that the loading process in the text is equivalent to $\frac{1}{2}M$ double transfers.

TABLE 5

α	M	Ratios of Successive Differences from Equilibrium Concentrations in Phase 1	
		From Equation (A22)	From Equations (A1)-(A5)
3·0	5	1·52	1·49
2·0	5	1·29	1·25
1·5	5	1·15	1·15
3·0	10	1·32	1·38
2·3	10	1·22	1·22
2·0	10	1·17	1·15
1·5	10	1·09	1·07
3·0	15	1·27	1·36
1·5	15	1·07	1·06
1·5	20	1·06	1·05

The solution of the boundary-value problem described by (A16)–(A19) is

$$u=e^{-2\beta(1-w)}+4\beta\sum_{n=1}^{\infty}\frac{z_n e^{\beta w}\sin[z_n(1-w)]e^{-(\beta^2+z_n^2)t}}{(\beta^2+z_n^2)\{-(1+\beta)\cos z_n+z_n\sin z_n\}}, \quad \ldots \textbf{(A20)}$$

where z_n are the roots of the equation

$$z\cot z+\beta=0. \quad \ldots\ldots\ldots\ldots\ldots \textbf{(A21)}$$

If the number of double transfers is reasonably large only the first term in the series need be retained. Also if β is large, as it is in practical cases, the first root of (A21) is approximately equal to $\beta\pi/(\beta+1)$. Thus (A20) becomes

$$u=e^{-2\beta(1-w)}+\frac{4\beta z e^{\beta w}\sin[z(1-w)]e^{-(\beta^2+z^2)t}}{(\beta^2+z^2)\{-(1+\beta)\cos z+z\sin z\}}, \quad \ldots \textbf{(A22)}$$

where

$$z=\beta\pi/(\beta+1). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(A23)}$$

Since the derivation of these equations involves many approximations it is desirable that they should be checked against correct values calculated directly from (**A1**)–(**A5**). An important quantity is the ratio by which the difference of the concentration from its equilibrium value is reduced by one double transfer. The value of this ratio for the first phase is shown in Table 5, as calculated from (**A22**) and also as derived from the correct calculations using (**A1**)–(**A5**). The values are in general agreement over a wide range of α and M. The variation of concentration with phase number is also given substantially correctly by (**A22**), as shown in Figures 4, 5, and 6. These comparisons indicate that (**A22**) gives a useful approximate description of the approach to equilibrium.

By solving (**A22**) for N we find that the number of double transfers required to bring the mole fraction of HA_1 in a given phase to the value m is given by

$$N=\frac{2(\alpha^2+1)}{(\alpha-1)^2}F(\beta,w,m), \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(A24)}$$

where

$$F(\beta,w,m)=\frac{\beta^2}{\beta^2+z^2}\ln\left(\frac{4\beta z e^{\beta w}\sin[z(1-w)]}{[(1-m)/m-e^{-2\beta(1-w)}](\beta^2+z^2)[-(1+\beta)\cos z+z\sin z]}\right) \quad \ldots\ldots\ldots\ldots \text{(A25)}$$

with β, z, w defined by (**A15**), (**A23**), (**A14**) respectively. These are the equations used in the text. Since w is the number of phases containing purified HA_2 divided by the number of phases required to contain all the HA_2, we can equate w to the fractional yield of purified HA_2.

REFLUX IN COUNTER-CURRENT DISTRIBUTION

II. THE PARTITION PROCESS

By A. F. BEECHAM* and V. W. MASLEN*

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Summary

A method is described of applying reflux to the separation of two solutes by counter-current distribution in a modified Craig tube system. Expressions are derived which relate the solute distribution at any stage to the number of transfers performed. The method is analysed in terms of the number of tubes and transfers required to effect separation. It is concluded that the process has a high theoretical resolving power but that its usefulness may be limited since its application entails repeated recovery of solute from end fractions. The distribution under reflux of *m*- and *p*-nitroaniline is described.

I. INTRODUCTION

The application of reflux to a counter-current distribution process for resolving mixtures of weak acids or bases has been described in Part I (Barker and Beecham 1960). This paper discusses a reflux process which may be used for any class of solute. Tube systems designed by Verzele and Alderweireldt (1954), von Metzsch (1959), and Wilhelm and Foos (1959) permit counter-current flow of both upper and lower phases in a distribution machine and using these it is possible to obtain reflux. The method is as follows. After loading is complete an upper-phase transfer is performed so that the upper phase from the first tube emerges from the system and lower phase only is left in the last tube. This is removed. The tubes are then equilibrated and the lower-phase transfer performed, after which the first tube contains only upper phase and the last only lower. The phases that have been removed are then evaporated to dryness (or dissolved material otherwise separated from solvent), the solutes transferred to the opposite liquid phases, and returned to the tube system at the ends from which they emerged. The tubes are again agitated, allowed to settle, and the whole operation repeated beginning with the upper-phase transfer. Such a sequence is conveniently termed a " double transfer ". The process is illustrated in Figure 1 for a 3 tube system.

II. THE EQUILIBRIUM STATE

For any solute the partition ratio, G, and the partition coefficient, P, are related as follows

$$G=PV, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where the volume factor, V, denotes the ratio of the volume of the upper phase to that of the lower. When $G>1$ it is evident that as refluxing proceeds the

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solute will become concentrated in the tubes nearest the end of the system at which the upper phase emerges, whereas with $G<1$ concentration will occur at the other end. Distribution will converge to a steady state at which, as is shown in Section III, the ratio of the quantities of a solute in any two adjacent tubes is $1 : G^2$ and

$$S_r = S_T \frac{1-G^2}{1-G^{2M}} \cdot G^{2M-2r}, \quad \ldots\ldots\ldots\ldots \quad (2)$$

where S_r is the amount of the solute S in the rth tube of an M-tube system and S_T is the total solute.

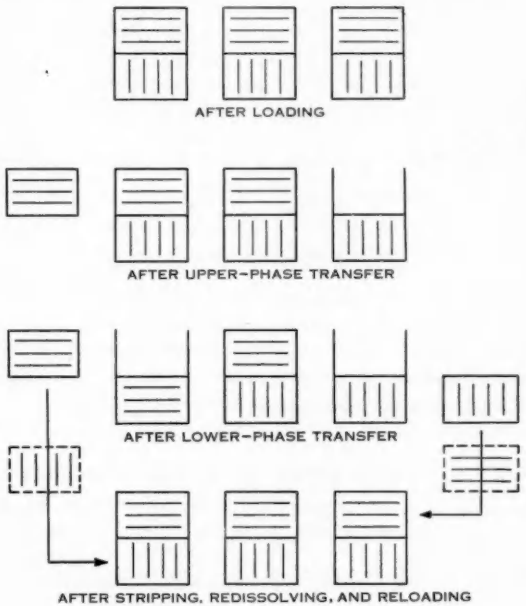

Fig. 1.—Schematic representation of a double transfer in the reflux process.

Figure 2 shows the steady-state distribution, calculated from equation (2), for various values of G in a 50 tube system. Unless M is small and G close to 1 the number of tubes has a negligibly small effect on the shape of the curves. In the separation in 50 tubes of a pair of solutes with G values of 1·1 and 0·9 ($\alpha=1\cdot2$ where $\alpha=P_A/P_B$) 99·5 per cent. of each can be recovered when the steady state is attained, each with a purity of 99·5 per cent. With two solutes in equal quantities and Gs of 1·05 and 0·95 ($\alpha=1\cdot1$) phase 1 contains 4·8 per cent. of the first (purity >99 per cent.) and phase 100, 4·8 per cent. of the second (of equal purity). If these phases are replaced by fresh solvent and refluxing

continued until the steady state is again reached, then phases 1 and 100 again have purities >99 per cent. and each contains 4·8 per cent. of the remainder of the appropriate solute. A solute pair with *Gs* of 1·01 and 0·99 would require 250 tubes to give end phases of the same purity.

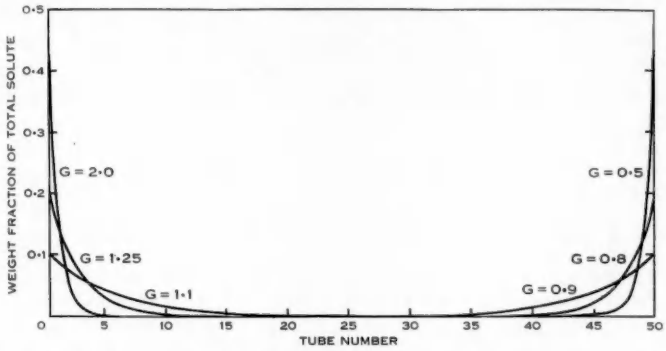

Fig. 2.—Steady-state distribution of solute in 50 tubes for various values of *G*.

III. The Double Transfer Number

It is apparent from Section II that the theoretical resolving power of the reflux process is considerable; however, it is necessary to know the number of double transfers required to effect a given distribution. This reduces to a problem of matrix algebra, by means of which we derive expressions relating the double transfer number to the distribution at any stage, after any form of loading. We then consider the case of uniform loading.

(*a*) *Formulation of the Matrix Problem*

If unit quantity of a solute *S* is distributed throughout an *M*-tube system and $S_{r,N}$ is the amount in tube *r* after *N* double transfers, then

$$\sum_{r=1}^{M} S_{r,N}=S_T=1, \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

and the upper and lower phases of tube *r* contain respectively the quantities $(G/1+G)S_{r,N}$ and $[1/(1+G)]S_{r,N}$. We consider successive stages of the $(N+1)$th double transfer. After transferring the upper phase and equilibrating we have

$$S_{r,N'}=\frac{1}{1+G}S_{r,N}+\frac{G}{1+G}S_{r+1,N} \quad r=1, 2, \ldots, (M-1), \quad \ldots. \quad (4a)$$

and

$$S_{M,N'}=\frac{1}{1+G}S_{M,N}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4b)$$

After the lower-phase transfer, return of solute and equilibration, we have

$$S_{r,N+1}=\frac{G}{1+G}S_{r,N'}+\frac{1}{1+G}S_{r-1,N'} \quad r=2, 3, \ldots, M, \quad \ldots\ldots \quad (5a)$$

and

$$S_{1,N+1}=\frac{G}{1+G}S_{1,N'}+\frac{G}{1+G}S_{1,N}. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5b)$$

Eliminating $S_{r,N'}$ from (5) we obtain the following relations between $S_{r,N+1}$ and $S_{r,N}$:

$$\begin{aligned}
(1+G)^2S_{1,N+1} &= G(2+G)S_{1,N}+G^2S_{2,N} \\
(1+G)^2S_{2,N+1} &= S_{1,N}+2GS_{2,N}+G^2S_{3,N} \\
\ldots\ldots &= \ldots\ldots\ldots \\
(1+G)^2S_{r,N+1} &= S_{r-1,N}+2GS_{r,N}+G^2S_{r+1,N} \\
\ldots\ldots &= \ldots\ldots\ldots \\
(1+G)^2S_{M,N+1} &= S_{M-1,N}+(1+2G)S_{M,N}
\end{aligned}$$

or in matrix notation,

$$\mathbf{S}_{N+1}=\mathbf{T}\mathbf{S}_N. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

The elements of $\mathbf{T}$ are independent of N and it follows, therefore, that

$$\mathbf{S}_N=\mathbf{T}\mathbf{S}_{N-1}=\mathbf{T}^N\mathbf{S}_0. \quad \ldots\ldots\ldots\ldots\ldots \quad (7)$$

where $\mathbf{S}_0$ is the column vector appropriate to the initial loading. The labour of computing $\mathbf{T}^N$, which is formidable, can be avoided as follows. Let λ_p, $\mathbf{y}_m$, $\mathbf{z}_n$ ($p, m, n=1, 2, \ldots, M$) be the eigenvalues, right-hand and left-hand eigenvectors respectively of the matrix $\mathbf{T}$, that is,

$$\mathbf{T}\mathbf{y}_m=\lambda_m\mathbf{y}_m, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

$$\mathbf{z}_n\mathbf{T}=\lambda_n\mathbf{z}_n. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

It may be shown that, for $m\neq n$,

$$\mathbf{z}_n\mathbf{y}_n=0,$$

and if $\mathbf{z}$ is suitably normalized, this orthogonality relation may be written

$$\begin{aligned}
\mathbf{z}_n\mathbf{y}_m &= 1 \qquad m=n, \\
&= 0 \qquad m\neq n.
\end{aligned} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

It is possible to expand arbitrary $\mathbf{S}_0$ in terms of $\mathbf{y}_m$. Normalizing according to (10)

$$\mathbf{S}_0=\sum_{m=1}^{M}(\mathbf{z}_m\mathbf{S}_0)\mathbf{y}_m. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

It follows from (7), (8), and (11) that

$$\mathbf{S}_N=\mathbf{T}^N\mathbf{S}_0=\sum_{m=1}^{M}(\mathbf{z}_m\mathbf{S}_0)\lambda_m^N\mathbf{y}_m. \quad \ldots\ldots\ldots \quad (12a)$$

Equivalently

$$S_{r,N}=\sum_{m=1}^{M}\sum_{p=1}^{M}z_{m,p}S_{p,0}\lambda_m^N y_{r,m}. \quad \ldots\ldots\ldots \quad (12b)$$

Thus, having found the eigenvectors and eigenvalues of $\mathbf{T}$, we can write the distribution functions $S_{r,N}$.

(b) Solution of Matrix Equations (8) *and* (9)*

For (8) and (9) to have a solution it is necessary that

$$\det | \mathbf{T}-\lambda_1 | =0,$$

that is,

$$I=\begin{vmatrix} G^2+G\beta & G^2 & & & & & \\ 1 & G\beta & G^2 & & & & \\ & 1 & G\beta & G^2 & & & \\ & & & 1 & G\beta & G^2 & \\ & & & & 1 & G\beta & G^2 \\ & & & & & 1 & 1+G\beta \end{vmatrix} =0, \quad \ldots\ldots\ldots \textbf{(13)}$$

where we have substituted $(G+1)^2\lambda=G(2-\beta)$. Expanding I, firstly by the first row and column, then by the last,

$$I=G^2\Delta_{M-2}+(1+G^2)\Delta_{M-1}+\Delta_M, \quad \ldots\ldots\ldots \textbf{(14)}$$

where

$$\Delta_M=\begin{vmatrix} G\beta & G^2 & & & & & \\ 1 & G\beta & G^2 & & & & \\ & 1 & G\beta & G^2 & & & \\ & & & 1 & G\beta & G^2 & \\ & & & & 1 & G\beta & \end{vmatrix} =G\beta\Delta_{M-1}-G^2\Delta_{M-2}.$$

$$\ldots\ldots\ldots\ldots \textbf{(15)}$$

Δ_M may be evaluated as follows. Define

$$f(t)=\sum_{n=0}^{\infty}\Delta_n t^n. \quad \ldots\ldots\ldots\ldots\ldots\ldots \textbf{(16)}$$

Then, according to (15)

$$(G^2t^2-G\beta t+1)f(t)=1,$$

that is,

$$f(t)=\sum_{n=0}^{\infty}\frac{t^nG^n\sin(n+1)\theta}{\sin\theta}, \quad \ldots\ldots\ldots\ldots \textbf{(17)}$$

where, in (17), we have put $\beta=2\cos\theta$.

Comparing (16) and (17)

$$\Delta_M=\frac{G^M\sin(M+1)\theta}{\sin\theta}.$$

It follows that

$$I=(1+G\beta+G^2)G^{M-1}\frac{\sin M\theta}{\sin\theta}. \quad \ldots\ldots\ldots\ldots \textbf{(18)}$$

An independent set of solutions of $I=0$ is, according to (18)

$$\beta_m=-2\cos m\theta,$$

* For fuller details of the techniques used in this subsection, see Hoffmann and Konya (1951) and Rutherford (1947).

where

$$\theta=\pi/M \qquad m=1, 2, \ldots, (M-1), \quad \ldots\ldots \textbf{(19a)}$$

$$\beta_M=-(1+G^2)/G, \quad \ldots\ldots \textbf{(19b)}$$

that is,

$$\lambda_m=\frac{2G(1+\cos m\theta)}{(1+G)^2} \quad m=1, 2, \ldots, (M-1), \quad \ldots. \textbf{(20a)}$$

$$\lambda_M=1. \quad \ldots\ldots \textbf{(20b)}$$

Substitution of the eigenvalues (**20**) into (**8**) and (**9**) gives the equations to be satisfied by the corresponding eigenvectors. Solutions of these equations are

$$y_{r,m}=G^{-r}\{G \sin (r-1)m\theta-\sin rm\theta\} \quad m=1, 2, \ldots, (M-1), \ldots \textbf{(21a)}$$

$$y_{r,M}=G^{2M-2r}, \quad \ldots\ldots \textbf{(21b)}$$

$$z_{m,r}=\frac{2G^r\{G \sin (r-1)m\theta-\sin rm\theta\}}{M(1-2G \cos m\theta+G^2)}, \quad \ldots\ldots \textbf{(22a)}$$

$$z_{M,r}=\frac{1-G^2}{1-G^{2M}}, \quad \ldots\ldots \textbf{(22b)}$$

where the **z** of (**22**) have been normalized according to (**10**). Equations (**20**)–(**22**) constitute the complete solution of the matrix problem.

(*c*) *The Distribution at Equilibrium*

It is clear from (**20a**) that, for $m \neq M$

$$0<\lambda_m<1.$$

Thus, as $N \to \infty$, $\lambda_m^N \to 0$ and the equilibrium distribution is given by

$$\begin{aligned} S_{r,\infty} &= \sum_{t=1}^{M} z_{M,t} S_{t,0} y_{r,M} \\ &= \frac{1-G^2}{1-G^{2M}} \left(\sum_{t=1}^{M} S_{t,0} \right) G^{2M-2r} \\ &= \frac{1-G^2}{1-G^{2M}} \cdot G^{2M-2r}, \quad \ldots\ldots \textbf{(22)} \end{aligned}$$

that is,

$$S_{1,\infty} : S_{2,\infty} : S_{3,\infty} : \ldots = 1 : G^{-2} : G^{-4} : \ldots$$

(*d*) *The Application of* (**12**) *to the Case of Uniform Loading*

The only part of (**12**) dependent on the manner of loading is the factor ($\mathbf{z}_m\mathbf{S}_0$). In the case of uniform loading

$$S_{r,0}=\frac{1}{M} \text{ for all } r, \quad \ldots\ldots \textbf{(23)}$$

so that

$$\mathbf{z}_m\mathbf{S}_0=\frac{1}{M}\sum_{t=1}^{M} z_{m,t}$$

$$=\frac{1}{M^2}\cdot\frac{2}{(1-2G\cos m\theta+G^2)}\sum_{t=1}^{M} G^t\{G\sin(t-1)m\theta-\sin tm\theta\}$$

$$=\frac{2G(G^2-1)\sin m\theta}{M^2(1-2G\cos m\theta+G^2)^2}\{1+(-1)^{m+1}G^M\}. \quad \text{..... (24a)}$$

$$\mathbf{z}_M\mathbf{S}_0=\frac{1-G^2}{1-G^{2M}}. \quad \text{..... (24b)}$$

Inserting (24) into (12),

$$S_{r,N}=\frac{(1-G^2)G^{2M-2r}}{1-G^{2M}}+\frac{2G^{1-r}(G^2-1)}{M^2}$$

$$\times\sum_{m=1}^{M-1}\frac{\sin m\theta\{G\sin(r-1)m\theta-\sin rm\theta\}\{1+(-1)^{m+1}G^M\}}{(1-2G\cos m\theta+G^2)^2}$$

$$\times\left\{\frac{2G(1+\cos m\theta)}{(1+G)^2}\right\}^N \quad \text{..... (25)}$$

$$=S_{r,\infty}+G^{-r}(GA_{r,N}-A_{r+1,N}+GC_{r,N}-C_{r+1,N}), \quad \text{..... (26)}$$

where

$$A_{r,N}=\frac{2G(G^2-1)(1+G^M)}{M^2}\sum_{m=1(2)}^{M-1}\frac{\sin m\theta\sin(r-1)m\theta}{(1-2G\cos m\theta+G^2)^2}\left\{\frac{2G(1+\cos m\theta)}{(1+G)^2}\right\}^N, \quad \text{..... (27a)}$$

$$C_{r,N}=\frac{2G(G^2-1)(1-G^M)}{M^2}\sum_{m=2(2)}^{M-1}\frac{\sin m\theta\sin(r-1)m\theta}{(1-2G\cos m\theta+G^2)^2}\left\{\frac{2G(1+\cos m\theta)}{(1+G)^2}\right\}^N. \quad \text{..... (27b)}$$

TABLE 1

M \ G	0·2	0·4	0·6	0·8	0·95
2	$2+1\cdot8n$	$1+2\cdot6n$	$3n$	$-2+3\cdot3n$	$-4+3\cdot3n$
5	$14+3\cdot3n$	$17+7\cdot6n$	$15+14n$	$4+20n$	$-15+23n$
10	$40+3\cdot8n$	$53+10\cdot1n$	$67+26n$	$57+62n$	$-24+91n$
15	$64+3\cdot8n$	$92+10\cdot8n$	$129+30n$	$154+98n$	$-4+198n$
20	$89+3\cdot9n$	$133+11\cdot0n$	$196+33n$	$275+124n$	$61+337n$
30	$142+3\cdot9n$	$217+11\cdot2n$	$336+34n$	$551+152n$	$352+677n$
45	$221+3\cdot9n$	$345+11\cdot3n$	$553+35n$	$1000+169n$	$1194+1227n$
60	$301+3\cdot9n$	$475+11\cdot3n$	$775+35n$	$1470+176n$	$2423+1714n$
90	$463+3\cdot9n$	$738+11\cdot3n$	$1227+35n$	$2443+181n$	$5552+2392n$

Except for small N (roughly $N<M$ but also depending on G) the series (**27**) converge quickly. Using the equilibrium and the first non-equilibrium terms of (**25**), N has been calculated for various M and G for close approach to the steady state in tube 1. If $G<1$ this tube contains least solute and approaches the steady-state value least rapidly. The results are listed in Table 1 in the form $N=A+Bn$, where $n=-\log\delta$, $S_{1,N}=S_{1,\infty}(1+\delta)$, and δ, the difference from the equilibrium value, is $\leqslant 0{\cdot}1$. The values below the heavy lines are accurate; elsewhere the two-term approximation is less good.

IV. The Separation of Two Solutes

Discussion in this section is restricted to the case of uniform loading, since the mathematics is thereby simplified and since it has been found that the number of double transfers required to attain a given distribution is not reduced by several other possible methods of loading. With uniform loading, if the total quantity of a solute S is unity, the amount in tubes 1 to r is

$$\Sigma_{r,N}(G)=\sum_{r=1}^{r} S_{r,N}=\frac{(1-G^{2r})G^{2M-2r}}{1-G^{2M}}-\frac{1}{G^r}\{A_{r+1,N}+C_{r+1,N}\}, \quad \ldots\ (28)$$

and the ratio of the quantities of two solutes with G_1 and G_2 in tubes 1 to r is

$$R=\frac{\Sigma_{r,N}(G_1)}{\Sigma_{r,N}(G_2)}. \quad \ldots\ (29)$$

With M fixed, one may plot R *against* N for several values of r, thus showing the rate of approach of R to its limiting value. Similar plots of Σ *against* N show the amount of solute of the corresponding purity which may be retrieved. To obtain a complete picture the process is repeated for several M. For the particular case of $G_1=G$, $G_2=1/G$ the calculations simplify considerably. Thus

$$\begin{aligned}\Sigma_{r,N}(1/G)&=\sum_{r=M+1-r}^{M} S_{r,N}(G)\\ &=\frac{1-G^{2r}}{1-G^{2M}}+G^{-(M-r)}\{A_{r+1,N}-C_{r+1,N}\}. \quad \ldots\ (30)\end{aligned}$$

Figures 3 and 4 show some results calculated from (**28**)–(**30**) for the cases $G_1=0{\cdot}75$, $G_2=1{\cdot}33$ and $G_1=0{\cdot}95$, $G_2=1{\cdot}05$. Both R and $\Sigma(G_1)+\Sigma(G_2)$, the total solute in tubes 1 to r, are plotted for $r=1$ and $r=\frac{1}{2}M$, for several values of M.

The graphs of R against N show that a purification may sometimes be more economically effected in steps rather than in a single operation. After the initial loading, reflux may be applied until the rate of change of R with N reaches a value judged to be too small to warrant further processing. The tubes to one side of the centre of the bank may then be emptied and the contents of the remainder distributed throughout the whole. If this distribution is uniform and a further N double transfers are performed, the ratio of the two solutes, in the same group of tubes as was first considered, is now R^2. Another distribution followed by N double transfers would give a ratio of R^3. If the tubes retained after the first distribution contain the quantities x and y of the two solutes (where $x+y=1$), after the third distribution these amounts are reduced to x^3

and y^3 and the purity is raised from $x/(x+y)$ to $x^3/(x^3+y^3)$. For example, if, with $G_1=0\cdot75$, $G_2=1\cdot33$, and 10 tubes, after the first step the contents of half the tubes, comprising $0\cdot1$ and $0\cdot9$ unit respectively of the two solutes, is twice

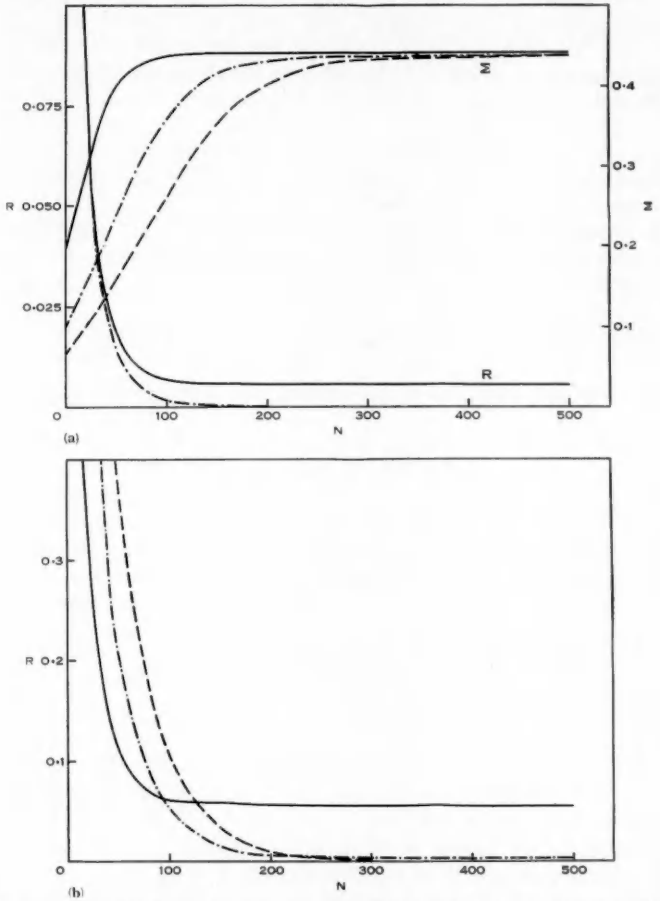

Fig. 3.—(*a*) Variation of R and of $\Sigma\{=\Sigma(G_1)+\Sigma(G_2)\}$ with N for the first tube of an M-tube system; $G_1=1/G_2=0\cdot75$, $M=10$ ——, $M=20$ ·—·, $M=30$ — —. (*b*) Variation of R with N for the first $\frac{1}{2}M$ tubes of an M-tube system; $M=10$ ——, $M=20$ ·—·, $M=30$ — —, $G_1=1/G_2=0\cdot75$. Σ, not shown, is constant and equal to unity.

reprocessed, the final quantities are $0\cdot001$ and $0\cdot729$ unit and the purity has been raised from 90 to 99·9 per cent. To obtain the same fraction of the total with the same degree of purity in a single run would require many more tubes and many more double transfers.

V. Discussion

It is interesting to compare some of the features of the reflux method with those of the Craig process. Under reflux the number of tubes containing a solute becomes less as the number of transfers increases, whereas in a Craig

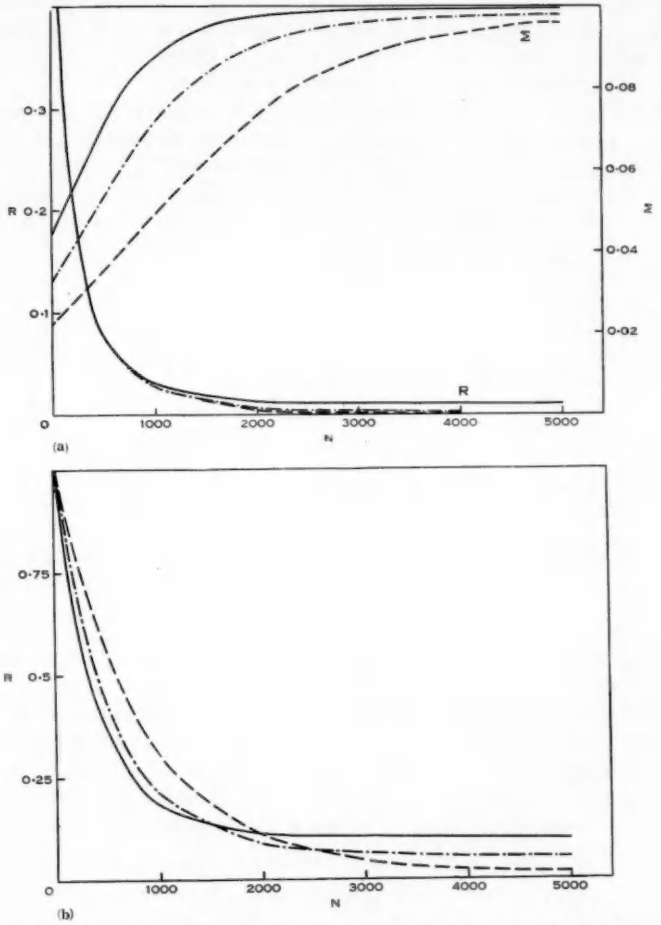

Fig. 4.—(*a*) Variation of R and of $\Sigma\{=\Sigma(G_1)+\Sigma(G_2)\}$ with N for the first tube of an M-tube system; $M=45$ ——, $M=60$ ·—·, $M=90$ — —, $G_1=1/G_2=0\cdot95$. (*b*) Variation of R with N for the first $\frac{1}{2}M$ tubes of an M-tube system, $M=45$ ——, $M=60$ ·—·, $M=90$ — —, $G_1=1/G_2=0\cdot95$. $\Sigma=1$ in this case.

distribution the solute band becomes broader. Thus a separation can be effected by reflux in fewer tubes than by the Craig method. Also, more material can be handled in a reflux separation than in a Craig. In the Craig process solute is

loaded into the first or the first few tubes of the battery, usually at a concentration sufficiently low for departure from ideality in partition behaviour to be small. This is necessary if α, the separation factor, is to remain constant as distribution proceeds. In the reflux method every tube may contain solute initially, in amount such that account is taken of the concentration increases to be expected in the end tubes as refluxing proceeds. The closer is α to unity, the greater can be the initial concentrations. In other words, the more difficult the separation, the more the material that can be treated in a single run.

In the reflux process, unlike the Craig, only two solutes can be separated in one run. It is necessary, too, that the G value of one be greater than unity and that of the other less. This condition can be satisfied by varying the volume ratio of the solvent phases or by adjusting their composition. Ideally the two G values should be reciprocal.

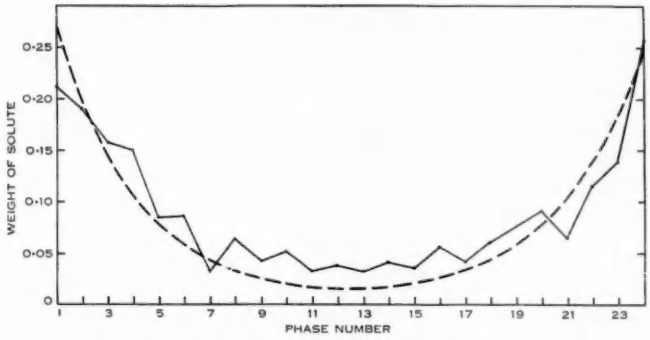

Fig. 5.—Distribution in 12 tubes of *m*-nitroaniline ($G=0\cdot75$) and *p*-nitroaniline ($G=1\cdot37$) after 65 double transfers. *m*-+*p*- at 65th double transfer (experimental) ⋀⋀; *m*-+*p*- at equilibrium (calculated for $G_m=0\cdot75, G_p=1\cdot33$) ——.

The number of transfers required to effect a given separation is roughly the same with both processes. For this reason, together with considerations of the number of tubes required and the amount of solute to be treated, the reflux process might be regarded as complementary to the Craig. However, the necessity for repeated isolation of solute from the emerging phases renders it unattractive from a practical point of view.

VI. Experimental

A mixture of benzene, chloroform, methanol, water (8 : 8 : 11 : 4) separated into two phases of equal volume. The partition coefficients of *m*- and *p*-nitroaniline in this system remained close to $0\cdot75$ and $1\cdot37$ over the concentration range $0\cdot1$–$0\cdot5$ per cent.

A mixture of 1 g *m*- and 1 g *p*-nitroaniline was dissolved in the solvent system, distributed uniformly through a bank of 12 Verzele tubes and subjected to reflux. The separation was followed by periodic weighing of the solute

contained in the emerging end phases. After 65 double transfers the weight in each of the 24 phases was determined. The result, shown in Figure 5, indicates that the distribution takes the predicted form.

VII. Acknowledgments

We thank Dr. J. A. Barker and Dr. A. C. Hurley for valuable discussions and Mr. J. Dods for technical assistance.

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LIQUID–VAPOUR EQUILIBRIA

X. THE SYSTEMS ACETONE+NITROMETHANE AND ACETONE+ACETONITRILE AT 45 °C

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Summary

Liquid-vapour equilibrium data are given for the systems acetone+nitromethane and acetone+acetonitrile at 45·00 °C. The data are used to calculate the excess free energy of mixing for these systems. The former system has a negative value of the excess free energy of mixing and shows a change in sign of the deviation of the activity of nitromethane from the Raoults law value at a mole fraction of acetone of 0·35. A value of the virial coefficient β_{12} in the equation of state of the mixed vapours was estimated from the equilibrium data for this system. The excess free energy of mixing for the system acetone+acetonitrile is zero within the experimental error over the whole concentration range.

The Stockmayer potential was used to calculate values of β_{12} for the binary systems formed from acetone, nitromethane, and acetonitrile. For the system acetone+nitromethane the value estimated from our data is more negative than the value calculated using the Stockmayer potential, indicating a specific interaction, possibly hydrogen bonding, between the acetone and nitromethane molecules.

I. Introduction

The liquid-vapour equilibria of the system acetone+acetonitrile has been measured at 760 mm Hg by Pratt (1947). No liquid-vapour equilibrium measurements have been reported for the system acetone+nitromethane. The present measurements were made to obtain values of the excess free energy of mixing for these systems at 45 °C for comparison with values obtained previously for other systems containing one or more of the same components.

II. Experimental

(*a*) *Apparatus*

The liquid-vapour equilibrium and vapour pressure measurements were made using the methods described by Brown and Smith (1959) but with water at 2 °C supplied to the condensers to prevent loss of acetone. The liquid and vapour samples for the system acetone+nitromethane were analysed by density measurements using the methods of Brown and Ewald (1950). Those for the system acetone+acetonitrile were analysed by refractive index measurements using a Hilger-Chance precision refractometer maintained at 25·00 °C.

(*b*) *Purification and Physical Properties of Components*

The acetonitrile, acetone, and nitromethane were purified by the methods of Brown and Smith (1954, 1955, 1957 respectively). The physical properties

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TABLE 1
PHYSICAL PROPERTIES OF COMPONENTS

Properties	Acetone	Nitromethane	Acetonitrile
$d_4^{25\cdot00}$	0·78424	1·13080	0·77656
$n_D^{25\cdot00}$	1·35599	1·37964	1·34151
Boiling point (°C/760 mm Hg) ..	56·06	101·02	81·56
Vapour pressure (45·00 °C, mm Hg)	512·72	93·72	208·35

of the liquids used are shown in Table 1. The vapour pressures of the liquids were checked at 45 °C and at the normal boiling point and found to be in good agreement with the values previously obtained by us.

TABLE 2
ACETONE + NITROMETHANE
Density : composition data

x_1	$d_4^{25\cdot00}$	x_1	$d_4^{25\cdot00}$
0·0519	1·10750	0·5020	0·93286
0·1000	1·08652	0·5929	0·90277
0·2021	1·04400	0·6972	0·86996
0·3050	1·00367	0·8179	0·83422
0·4251	0·95960	0·9117	0·80789
0·4999	0·93346	0·9512	0·79720

TABLE 3
ACETONE + ACETONITRILE
Refractive index : composition data

x_1	$n_D^{25\cdot00}$	x_1	$n_D^{25\cdot00}$
0·060	1·34287	0·598	1·35184
0·105	1·34381	0·602	1·35192
0·210	1·34586	0·700	1·35311
0·297	1·34739	0·795	1·35410
0·389	1·34888	0·904	1·35516
0·486	1·35034	0·962	1·35568
0·521	1·35082		

(c) *Analytical Methods*

Mixtures were prepared from weighed amounts of the components, and their compositions were calculated allowing for air buoyancy and for the weight of air-vapour mixture of the first component displaced on adding the second; their compositions and refractive indices or densities are given in Tables 2 and 3. The method of Brown and Smith (1954) was used to calculate the composition of the liquid and vapour samples.

III. Results

The liquid-vapour equilibrium data are given in Tables 4 and 5 where x_1 and y_1 are the mole fractions of acetone in the liquid and vapour respectively, P is the total pressure in standard mm Hg, and α is the relative volatility given by $\alpha = y_1 x_2 / y_2 x_1$.

Table 4

ACETONE + NITROMETHANE 45 °C

Experimental results and derived thermodynamic functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0528	0·2190	114·44	5·030	—33·2	+ 1·7	— 0·1
0·0810	0·3048	125·28	4·974	—37·3	+ 2·5	— 0·7
0·1262	0·4165	142·75	4·942	—37·5	+ 3·5	— 1·7
0·2068	0·5607	173·81	4·896	—37·7	+ 3·8	— 4·8
0·3080	0·6846	213·24	4·877	—35·2	+ 1·8	— 9·6
0·4027	0·7677	251·17	4·902	—30·0	— 3·4	—14·1
0·4056	0·7701	252·35	4·909	—29·6	— 4·1	—14·4
0·4926	0·8272	288·40	4·931	—24·5	— 8·2	—16·2
0·5336	0·8503	305·56	4·965	—21·9	—13·0	—17·7
0·6134	0·8885	339·89	5·022	—16·5	—21·2	—18·3
0·7036	0·9235	379·48	5·085	—11·2	—30·9	—17·0
0·8017	0·9547	423·46	5·213	— 5·7	—48·8	—14·2
0·9037	0·9805	469·66	5·358	— 1·5	—70·3	— 8·1

Table 5

ACETONE + ACETONITRILE 45 °C

Experimental results and derived thermodynamic functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·052	0·120	225·3	2·48	+24	0	+ 1
0·095	0·206	239·9	2·47	+25	+ 2	+ 4
0·192	0·367	268·5	2·44	+14	— 2	+ 1
0·305	0·510	302·7	2·37	+ 3	+ 1	+ 2
0·403	0·611	331·7	2·33	— 3	+ 5	+ 2
0·481	0·682	355·2	2·31	— 3	+ 7	+ 2
0·606	0·781	393·2	2·31	— 2	+ 3	0
0·706	0·849	423·6	2·33	0	— 4	— 1
0·807	0·904	454·1	2·25	— 2	+15	+ 2
0·896	0·951	481·4	2·25	0	+13	+ 1

IV. Derived Thermodynamic Functions

The excess chemical potentials μ_1^E and μ_2^E and the excess free energy of mixing G_x^E were calculated from the equilibrium data using equations (**1**), (**2**), and (**3**). The values obtained (cal/g-mol) are given in Tables 4 and 5.

$$\mu_1^E = RT \ln (Py_1/P_1x_1) + (\beta_{11} - V_1)(P - P_1) + P\delta_{12}y_2^2, \quad \ldots\ldots \quad (1)$$

$$\mu_2^E = RT \ln (Py_2/P_2x_2) + (\beta_{22} - V_2)(P - P_2) + P\delta_{12}y_1^2, \quad \ldots\ldots \quad (2)$$

$$G_x^E = x_1\mu_1^E + x_2\mu_2^E, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where P_1 and P_2 are the vapour pressures of the pure components, β_{11}, β_{22}, and β_{12} are the second virial coefficients in the equation of state for the mixed vapours,

$$PV/RT=1+(y_1^2\beta_{11}+2y_1y_2\beta_{12}+y_2^2\beta_{22})\frac{1}{V}+\ldots,$$

and where

$$\delta_{12}=2\beta_{12}-\beta_{11}-\beta_{22}.$$

The liquid molar volumes V_1 and V_2 required for these calculations were obtained from density data given by Timmermans (1950). The values of the second virial coefficient for acetone and acetonitrile were obtained from the data of Lambert *et al.* (1949) and that for nitromethane from the equation given by McCullough *et al.* (1954).

(*a*) *Acetone+Nitromethane*

For this system no measured values of β_{12} or δ_{12} were available so values were estimated in the following way. Preliminary values of μ_1^E and μ_2^E were first calculated using corrections for the deviations of the vapours but with $\delta_{12}=0$ and the values obtained were tested for thermodynamic consistency by measuring the areas above and below datum under a plot of $(\mu_1^E-\mu_2^E)$ against x_1. These were found to correspond to $+5{\cdot}6$ cal/mol and $-23{\cdot}8$ cal/mol which gives a value of $-18{\cdot}2$ cal/mol for the integral

$$\int_0^1(\mu_1^E-\mu_2^E)\mathrm{d}x.$$

It was also found that the maximum in the plot of μ_2^E against x_1 was not at the same mole fraction as the minimum in the corresponding plot of μ_1^E. This means that the preliminary calculated values of the excess chemical potentials are not thermodynamically consistent due either to non-equilibrium conditions in the still or to the neglect of the mixture virial coefficient corrections. Previous data, obtained with the equilibrium still used in this work, for a number of other systems have been found to be thermodynamically consistent when reasonably accurate, measured or estimated values for the virial coefficients of pure and mixed vapours were used. Some of these systems had relative volatilities considerably higher than the values found here. It is therefore probable that the inconsistency of the preliminary values of the excess chemical potentials is mainly due to the neglect of corrections for the mixture virial coefficients.

A value of δ_{12} was then found by trial and error that reduced the value of the above integral to zero. This value was found to be $-2{\cdot}90$ l/mol. The final values of μ_1^E and μ_2^E given in Table 4 were calculated using the following values of the liquid molar volumes and virial coefficients (l/mol):

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
$-1{\cdot}66$	$-3{\cdot}11$	$-3{\cdot}83$	$-2{\cdot}90$	$0{\cdot}076$	$0{\cdot}056$

These final values showed that the maximum in μ_2^E was at the same mole fraction as the minimum in μ_1^E. As a further check on the consistency of the measured

x, y, and P data, Barker's (1953) method was used to calculate values of μ_1^E, μ_2^E, and G_x^E from the x and P values alone using the listed values for the virial coefficients and molar volumes. This gave the following expression for G_x^E:

$$G_x^E = x_1 x_2[-62 \cdot 5 - 36 \cdot 9(x_1 - x_2)].$$

Values of P, μ_1^E, μ_2^E, G_x^E, and y calculated from this expression were compared with the experimental and derived values given in Table 4 and the agreement was found to be good. The standard deviations were, respectively : 0·09 mm Hg, 2·3, 2·9, 1·3 cal/mol, and 0·0014 in mole fraction.

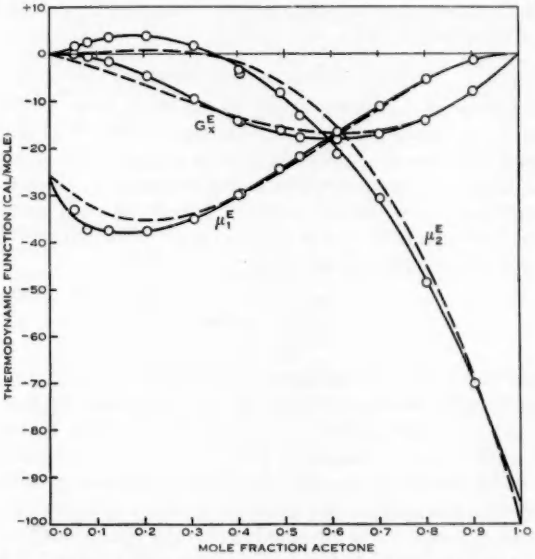

Fig. 1.—Thermodynamic functions : acetone+nitromethane 45 °C.
○—○ Experimental values from P, x, y data.
--- Values from P, x data. $G_x^E = x_1 x_2[-62 \cdot 5 - 36 \cdot 9(x_1 - x_2)]$.

The errors in the value of G_x^E due to those in the measured quantities were estimated to be ± 3 cal/mol. Graphs of the thermodynamic functions obtained by the two methods are shown in Figure 1.

This system shows an appreciable negative value of G_x^E and shows a change in sign of the deviation of the activity of nitromethane from the Raoult's law value at a mole fraction of acetone of about 0·35.

(*b*) *Acetone+Acetonitrile*

In the measurements on this system the accuracy of analysis of the liquid and vapour samples was reduced due to the small difference between the refractive indices (and other physical properties) of the components. Again no value

of β_{12} or δ_{12} has been measured for this system and a correction for the vapour deviations was made assuming $\delta_{12}=0$. The values of the liquid molar volumes and second virial coefficients used in calculating values of the thermodynamic functions for this system were as follows:

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
−1·66	−4·50	(−3·08)	0	0·076	0·050

The values of the derived thermodynamic functions are shown in Table 5. A plot of $(\mu_1^E-\mu_2^E)$ against x_1 showed the areas above and below datum to be approximately equal, but this test of thermodynamic consistency was not conclusive due to scatter of some of the points by about ±5 cal/mol.

The estimated maximum errors in the derived functions due almost entirely to errors in the compositions were found to be of the same order as the small values of the functions themselves. Thus the excess-free energy of mixing for this system is zero within the experimental error over the whole of the concentration range. This is in agreement with the results of Pratt (1947). A similar result was found by Brown and Smith (1955) for the system nitromethane+acetonitrile at 60 °C.

V. Discussion

For the system acetone+nitromethane our results indicate a change in sign of the deviation of the activity of nitromethane from the Raoult's law value at a mole fraction of acetone of 0·35 as is shown in Figure 1. The validity of this conclusion depends on the accuracy of our equilibrium data and on the reliability of the estimate that β_{12} has a value at 45 °C of −3·83 l/mol. Similar behaviour has been shown by McGlashan and Wingrove (1956) for the components of the mixture benzene+bromobenzene at 80 °C.

The value of the coefficient β_{12} estimated for this system, namely −3·83 l/mol, is more negative than either β_{11} or β_{22}. This kind of behaviour is not unique; it is shown, for example, by the systems diethyl ether+chloroform (Fox and Lambert 1951) and dioxane+chloroform (McGlashan and Rastogi 1958). Both of these systems resemble acetone+nitromethane in that they have negative heats of mixing.

It was suggested by Douslin (personal communication) that a value of the second virial coefficient for mixed vapours of polar molecules could be calculated using the Stockmayer potential (Stockmayer 1941) and employing suitable mixture rules.

The Stockmayer equation can be written in the form

$$\beta=b_0B^*(\tau,t),$$

where $b_0=\frac{2}{3}\pi\sigma^3$, $\tau=T/\theta$, $\theta=\varepsilon/k$, and $t=\mu^2/\varepsilon\sigma^3\sqrt{8}$, and where ε is the depth of the potential well, σ is the collision diameter, and μ is the dipole moment. Values of the function B^* have been tabulated by Hirschfelder, Curtiss, and Bird (1953) for values of t up to 1·5 and by Barker and Smith (1960) for t from 1·6 to 2·4.

For nitromethane values of the parameters θ, b_0, and t have been evaluated by Douslin and Waddington (1955) from the vapour pressure, vapour heat capacity, and heat of vaporization data of McCullough *et al.* (1954) and these lead to a calculated value of μ in good agreement with measured values.

TABLE 6
STOCKMAYER PARAMETER VALUES

Compound	Stockmayer Parameters			Second Virial Coefficients (45 °C l/mol)		Dipole Moment (D)	
	θ (°K)	t	b_0 (l/mol)	Calc.	Meas.	Calc.	Meas.
Acetone ..	479·0	0·8	0·06281	—1·57	—1·66	2·74	2·88
Nitromethane	290·4	1·6	0·09078	—3·11	—3·11	3·61	3·54
Acetonitrile	219·0	2·2	0·1060	—4·08	—4·50	3·98	3·96

For acetone, values of the parameters have been evaluated by Douslin (personal communication) from the second virial coefficient data of Lambert *et al.* (1949) and that of Pennington and Kobe (1957). For acetonitrile values have been evaluated by Barker (1959) from the second virial coefficient data of Lambert *et al.* (1949). These data are shown in Table 6 together with calculated and measured values of the dipole moments and the second virial coefficients at 45 °C for the pure component vapours.

TABLE 7
VALUES OF β_{12} AND δ_{12} CALCULATED FROM THE STOCKMAYER POTENTIAL

System	β_{12} (l/mol)	δ_{12} (l/mol)
Acetone+nitromethane ..	—2·00	+0·68
Acetone+acetonitrile	—4·10	+1·55
Acetonitrile+nitromethane ..	—3·48	+0·23

Values of the coefficient β_{12} were calculated from the Stockmayer parameter values listed in Table 6 using the following averaging rules.

$$b_{0_{12}}=[\tfrac{1}{2}(b_{0_{11}}{}^{\frac{1}{3}}+b_{0_{22}}{}^{\frac{1}{3}})]^3,$$
$$\theta_{12}=(\theta_{11}\cdot\theta_{22})^{\frac{1}{2}},$$
$$(b_0t\theta)_{12}=[(b_0t\theta)_{11}\cdot(b_0t\theta)_{22}]^{\frac{1}{2}}.$$

The first two are generally used in connection with the forces between non-polar molecules (see for example, Guggenheim 1952); and the third expresses the fact that the electrostatic interaction between two like or unlike molecules is proportional to the product of their dipole moments. The calculated values of β_{12} and the corresponding values of δ_{12} are shown in Table 7.

For the system acetone+nitromethane the value of $\delta_{12} = +0{\cdot}68$ l/mol estimated using the Stockmayer potential is much more positive than the value $-2{\cdot}90$ l/mol estimated from our equilibrium data. If the latter value is correct, it indicates that there is a specific interaction in addition to the dipole-dipole interaction between acetone and nitromethane molecules. This may involve hydrogen bonding between oxygen of acetone and hydrogen of nitromethane. This is made more plausible by the negative values of the heat of mixing and volume change on mixing. $H^m = -163$ j/mol (Brown and Fock 1957). $V^m = -0{\cdot}255$ ml/mol (Brown and Smith, unpublished data). A similar interaction is indicated for the system acetone+acetonitrile.

The conclusions reached in this paper must, however, remain tentative until experimental values for δ_{12} for these systems have been measured.

VI. Acknowledgments

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THE VARIABLE ELECTRONEGATIVITY METHOD

VI. AZULENE

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Summary

Results of a variable-electronegativity SCF treatment of azulene, using the method used in previous VESCF studies, are reported. A slightly more elaborate method in which non-neighbour core resonance integrals are included has also been used. The π-electron distributions obtained by these methods correspond to dipole moments of 1·85 and 1·33 D respectively, the experimental value being about 1 D.

The calculated bond orders accord with the rather incomplete experimental data on bond lengths. The π-electron densities account for the relative chemical reactivities of the azulene positions. The ionization potentials and proton magnetic resonance spectrum of azulene are also briefly considered.

The concept of electronegativities of conjugated atoms in non-alternant systems is discussed in some detail on the basis of the VESCF results. It is shown that the assumption that the electronegativity of a carbon atom depends only on its π-electron density is an oversimplification for non-alternant systems.

I. Introduction

The variable electronegativity method has hitherto been applied to heterocyclic systems (Brown and Heffernan 1958, 1959*a*, 1959*b*, 1959*c*, 1959*d*) and it is of interest to examine the VESCF treatment of non-alternant hydrocarbons. Azulene was chosen because its properties have now been studied in some detail, while both the conventional SCF (Julg 1955) and the semi-empirical configuration interaction (Pariser 1956*b*) molecular-orbital treatments are available for comparison. The dipole moment is of particular interest because it is probably the most direct indication of the non-uniformity of the π-electron distribution. It is widely recognized that the simple Hückel method grossly exaggerates this non-uniformity and that the more elaborate procedures reduce this distortion (Wheland and Mann 1949; Julg 1955; Pariser 1956*b*). It might be expected that the VESCF method would still further improve the agreement between the calculated and the observed moment.

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II. Method

The VESCF technique has been described fully in previous papers of the series.* The geometry of azulene is not accurately known but the length of the 9 : 10 bond is probably (Heilbronner, quoted by Scherr 1953 ; Robertson *et al.* 1958) 1·45 A and the remaining bonds are around the normal aromatic length. For the present calculations it was assumed when computing close interaction terms that the peripheral bond lengths are 1·390 A and that the central common bond length is 1·45 A. However, in the calculation of all the non-neighbour internuclear distances a simpler geometrical model of azulene, as used by Pariser (1956*b*), with all bonds of equal lengths (1·39 A) and the five- and seven-membered rings regular polygons with ring angles of 108° and 128° 34′ respectively, was employed. This simplified the computation of non-neighbour interaction terms and the error thus introduced is negligible compared with those arising from other approximations of the SCFMO technique.

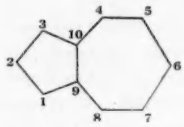

Table 1

INTERATOMIC DISTANCES AND COULOMB REPULSION INTEGRALS

μ,ν	Distance (A)	$\gamma_{\mu\nu}$ (eV)	μ,ν	Distance (A)	$\gamma_{\mu\nu}$ (eV)
1,2	1·390	7·351	2,6	5·211	2·759
9,10	1·450	7·226	3,4	2·443	5·407
2,9	2·249	5·727	3,5	3·765	3·698
5,10	2·509	5·303	1,6	4·525	3·083
6,9	3·140	4·405	1,5	4·466	3·121
2,4	3·582	3·886	1,4	3·622	3·843
2,5	4·622	3·024			

Values used for the coulomb repulsion integrals, $\gamma_{\mu\nu}$, are listed in Table 1. The values used for the core resonance integrals, $\beta_{\mu\nu}$, obtained from the extrapolation formula of Pariser and Parr (1953*a*), were −2·39 eV for the peripheral bonds and −1·691 eV for the central bond. The calculations were carried through using two different sets of assumptions :

(i) The above values of $\beta_{\mu\nu}$ were used and neutral atom penetration integrals were neglected. This procedure has been designated method BP in previous papers. However, for a hydrocarbon system, as noticed by Julg and Pullman

* The following notation is used in the text and tables of the present paper :
Z_μ, effective nuclear charge for the atomic orbital χ_μ,
P_μ, π-electron density on atom μ,
$P_{\mu\nu}$, bond order between atoms μ and ν,
I_μ, valence-state ionization potential of atom μ,
α_μ, core resonance integral of atom μ,
$F_{\mu\nu}$, Hartree-Fock Hamiltonian matrix element between atomic orbitals χ_μ and χ_ν.
A full discussion of these quantities has been given in previous papers of this series, or in references cited therein.

(1955), the penetration integral correction is practically the same for all atoms of the conjugated system when hydrogen atom penetrations are included. Thus for calculations of quantities which depend only on differences in values of diagonal Hamiltonian matrix elements $F_{\mu\mu}$, for example, π-electron densities, the results obtained will be virtually identical with those obtained by method AP, in which theoretical values for penetration integrals are included.

(ii) In addition to integral values assumed in method (i), core resonance integrals for non-neighbours, evaluated as described below, were included (the usual practice in this type of calculation has been to ignore all but nearest-neighbour core resonance integrals (Pariser and Parr 1953*a*, 1953*b*; McWeeny and Peacock 1957; Brown and Heffernan 1958)). Although the original studies of Pariser and Parr showed that reasonable agreement between calculated and observed spectroscopic properties of conjugated systems was obtained when non-neighbour resonance integrals were neglected, it has been shown more recently (Parr 1958) that improved agreement for a greater variety of experimental data can be obtained by including such integrals, at least in the case of benzene. The empirical Pariser-Parr formula relating resonance integrals and bond lengths is unlikely to be reliable for larger internuclear separations and therefore the alternative empirical procedure of assuming proportionality to overlap integrals (Mulliken 1950; Van Dranen and Ketelaar 1949, 1950; Simonetta, Favini, and Carra 1958) was employed. In this we write

$$\beta_{\mu\nu}=S_{\mu\nu}\beta_{1\cdot39}/S_{1\cdot39},$$

where the subscripts $1\cdot39$ indicate benzene bond values and $\beta_{1\cdot39}=-2\cdot39$ eV, the Pariser-Parr value. From this formula the following values (eV) of non-neighbour integrals were derived:

$$\beta_{13}=\beta_{29}=\beta_{2\cdot10}=-0\cdot470,$$
$$\beta_{24}=-0\cdot317,$$
$$\beta_{35}=\beta_{38}=\beta_{46}=\beta_{57}=-0\cdot278,$$

and all remaining non-neighbour $\beta_{\mu\nu}$ were neglected.

The final values of the quantities which were assumed to be functions of the effective nuclear charge, Z_μ, are listed in Table 2, while Tables 3 and 4 give the final VESCF Hamiltonian matrices by the two methods when convergence to the third decimal in the π-electron densities had been attained. For the actual calculations the Hamiltonian matrix was of course reduced to submatrices of orders 6 and 4 by using the symmetry properties of the molecule.

III. π-Electron Densities and Bond Orders

The π-electron densities and nearest-neighbour bond orders, calculated by the two procedures, are given in Table 5, together with the results obtained in previous ASMO calculations. All four sets of values of π-electron densities show the same qualitative order of positions and so all four sets account for the observed relative reactivities of the positions towards electrophils and nucleophils, as already noted for the previous results by Julg and Pariser.

The bond orders of the peripheral bonds are virtually identical with the benzene bond order, hence on this basis the assumption of the benzene bond length for these bonds is internally consistent. If a curve is constructed to pass through the points 1, 1·338; 0·667, 1·397; 0, 1·466, corresponding to the bond orders and bond lengths (Brown 1959; Costain and Stoicheff 1959) of ethylene, benzene, and a single bond between sp^2-hybridized carbon atoms, then from it and the bond order of the central bond, the length of the latter is predicted to be about 1·45 A. This again is consistent with the geometry assumed for the calculations.

TABLE 2

VALUES OF VESCF QUANTITIES (ev)*

Quantity	(i)	(ii)	Quantity	(i)	(ii)	Quantity	(i)	(ii)
Z_1	3·2285	3·2295	I_1	11·294	11·305	α_1	—56·602	—56·613
Z_2	3·2487	3·2546	I_2	11·525	11·592	α_2	—54·280	—54·347
Z_4	3·2720	3·2665	I_4	11·792	11·729	α_4	—59·046	—58·983
Z_5	3·2468	3·2458	I_5	11·503	11·492	α_5	—55·464	—55·453
Z_6	3·2637	3·2605	I_6	11·696	11·660	α_6	—54·739	—54·702
Z_9	3·2464	3·2507	I_9	11·499	11·548	α_9	—64·297	—64·346

* Except values of Z_μ, which are dimensionless.

IV. DIPOLE MOMENT

One of the most interesting features of non-alternant hydrocarbons such as azulene is that they have appreciable dipole moments. In the case of azulene an experimental value of the order of 1 D has been reported (Wheland and Mann 1949). However, this value may be somewhat uncertain as it was determined in solution in benzene using the molar refraction of naphthalene as an allowance for the distortion polarization. The moment for the molecule in the vapour phase is probably a few tenths of a Debye unit greater than the solution value.

On the theoretical side, the value calculated by the simple Hückel MO method is about 6 D. The situation was improved by applying the SCF and configuration-interaction techniques to the calculation of the moment, Pariser finding a value of 1·88 D and Julg a value of 1·70 D. The improvement in the calculated value obtained in these calculations must undoubtedly be attributed to the more detailed treatment of electron repulsion included in these more refined methods, the simple Hückel method greatly over-estimating the extent of charge separation. The VESCF method of calculating the π-electron distribution might be expected to lead to a still smaller preferential accumulation of electronic charge in the five-membered ring at the expense of the seven-membered ring because the value of the ionization potential, I_μ, which predominantly determines the relative electron-attracting power of an atom, is lowered as the electron density at atom μ is increased; in the other methods a constant value is adopted for I_μ.

The value of the dipole moment calculated from the VESCF charge distributions given in Table 5 and the assumed geometrical parameters mentioned above

TABLE 3

FINAL VESCF HAMILTONIAN MATRIX OBTAINED BY METHOD (i) (ev)

Numbers in parentheses indicate the azulene position corresponding to a row or column of the matrix

	(2)									
(2)	−5·6991	(3)								
(3)	−4·7923	−5·7804	(10)							
(10)	0·0269	−4·7379	−6·0823	(4)						
(4)	0·4603	−0·0362	−4·6339	−6·4097	(5)					
(5)	−0·0033	0·3961	0·0464	−4·8103	−6·5580	(6)				
(6)	−0·2504	−0·0331	0·5334	−0·1625	−4·7717	−6·5870	(7)			
(7)	−0·0033	−0·2778	0·0200	0·5746	0·0448	−4·7717	−6·5580	(8)		
(8)	0·4603	0·1322	−0·5995	0·1665	0·5746	−0·1625	−4·8103	−6·4097	(9)	
(9)	0·0269	0·7603	−2·3984	−0·5995	0·0200	0·5334	0·0464	−4·6339	−6·0823	(1)
(1)	−4·7923	0·2454	0·7603	0·1322	−0·2778	−0·0331	0·3961	−0·0362	−4·7379	−5·7804

TABLE 4

FINAL VESCF HAMILTONIAN MATRIX OBTAINED BY METHOD (ii) (ev)

	(2)*									
(2)	−5·8613	(3)								
(3)	−4·7816	−5·9095	(10)							
(10)	−0·4809	−4·7438	−6·1419	(4)						
(4)	0·4720	−0·3543	−4·6563	−6·3641	(5)					
(5)	−0·0002	0·4086	−0·2213	−4·7934	−6·4532	(6)				
(6)	−0·2570	−0·0401	0·5282	−0·4100	−4·7758	−6·4674	(7)			
(7)	−0·0002	−0·2842	0·0053	0·5738	−0·2258	−4·7758	−6·4532	(8)		
(8)	0·4720	0·1535	−0·8695	0·1433	0·5738	−0·4100	−4·7934	−6·3641	(9)	
(9)	−0·4809	0·2728	−2·3619	−0·8695	0·0053	0·5282	−0·2213	−4·6563	−6·1419	(1)
(1)	−4·7816	−0·2415	0·2728	0·1535	−0·2842	−0·0401	0·4086	−0·3543	−4·7438	−5·9095

* See subheading to Table 3.

is 1·85 D for method (i) and 1·33 D for method (ii). Thus the value obtained by method (i) is very close to values found in the previous more elaborate calculations, while the inclusion of non-neighbour resonance integrals brings the value considerably closer to that observed experimentally.

The calculated values for azulene are, more than is usually experienced, sensitive to the assumed geometry of the molecule. Thus if more precise geometrical information is obtained experimentally somewhat different values for the dipole moment may well be derived from the π-electron distribution calculated by the VESCF method. Nevertheless the present calculations account reasonably well for the observed dipole moment, and the improvement which results from including non-neighbour resonance integrals yields the best agreement with observation yet obtained for the dipole moment of azulene.

TABLE 5

π-ELECTRON DENSITIES AND BOND ORDERS

μ,ν*	(i)	(ii)	Julg	Pariser
2,2	1·004	0·988	0·997	0·979
3,3	1·061	1·059	1·049	1·096
9,9	1·009	0·998	1·042	1·013
4,4	0·937	0·954	0·908	0·879
5,5	1·009	1·011	1·034	1·049
6,6	0·961	0·969	0·938	0·948
1,2	0·657	0·651	—	0·660
1,9	0·632	0·640	—	0·610
4,10	0·617	0·617	—	0·611
9,10	0·196	0·186	—	0·288
4,5	0·656	0·654	—	0·651
5,6	0·648	0·649	—	0·648

* Subscripts to $F_{\mu\nu}$.

V. PROTON MAGNETIC RESONANCE SPECTRUM OF AZULENE

Schneider, Bernstein, and Pople (1958) compared the NMR shifts for protons attached to the different ring positions of azulene with the π-electron densities calculated by Pariser (1956*b*). They were not able to account fully for the observations, particularly the relative values of shifts for the 2- and 6-positions. It was thought initially that our VESCF π-electron densities would provide a better basis for interpretation of the chemical shifts but a direct comparison of the VESCF data with the observed shifts, along the lines of the comparison made by Schneider, Bernstein, and Pople, still did not lead to a complete explanation of the observations. However, Schneider, Bernstein, and Pople did not allow for the effect of variation in the hybridization of ring carbon atoms. A more detailed analysis of the factors influencing proton shifts has therefore been undertaken and it is hoped to report more fully on the NMR spectrum of azulene in a subsequent paper.

VI. Ionization Potentials

The results of calculation of the π-electron ionization potentials by the VESCF method are summarized in Table 6. The experimental values have not yet been reported but there are reasons for believing that the theoretical methods over-estimate the ionization potentials by 1 or 2 eV (Brown and Heffernan 1959*b*). In contrast to some of the heterocyclic systems studied in previous papers there are no *n*-electrons to be considered when dealing with ionization of the molecule; the smallest ionization potential to be observed experimentally will certainly correspond to ionization of a π-electron and so can be compared immediately with the data in Table 6.

Table 6

π-electron ionization potentials (ev)

Method	1st	2nd	3rd	4th	5th
(i)	10·04	10·86	13·39	13·91	15·54
(ii)	9·32	10·32	13·20	14·27	16·56

VII. Parameters for the Hückel MO Method

In the simple Hückel method all carbon atoms are assigned the same coulomb integral, α°, all carbon-carbon bonds the same resonance integral, β°, and non-neighbour interactions are ignored. Although a satisfactory explanation of relative chemical reactivities can be obtained on this basis, the charge distribution, judged on the basis of the calculated dipole moment, is grossly in error. However, a Hückel treatment in which the coulomb and resonance integrals are derived from VESCF matrix elements (expressed perhaps in "Hückel units"* by dividing by β^0 which is about −4·79 eV) would of course reproduce the VESCF

* As was briefly indicated in Part IV (Brown and Heffernan 1959*c*), the most satisfactory view of simple Hückel calculations seems to be that they roughly reproduce the results of VESCF calculations of *wave functions* (cf. McWeeny and Peacock 1957). In the Hückel method it has been customary to express the Hamiltonian matrix elements in units of β^0, that is, of the Hückel resonance integral of a benzene bond. It seems appropriate to call such a unit a "Hückel unit". In the VESCF method the Fock Hamiltonian matrix elements are normally expressed in more fundamental energy units such as eV. To make the VESCF matrix have the same appearance as the simple Hückel matrix, and especially to facilitate numerical comparisons of the two, one must express the VESCF elements in terms of the Fock Hamiltonian matrix element of a benzene bond F_{12} (benzene), that is, according to the current estimate of this matrix element (McWeeny and Peacock 1957) in units of −4·79 eV. When the VESCF matrix is given in such units it again seems appropriate to say that it is given in Hückel units.

It should be noted that when β^0 is evaluated by comparing spectroscopic intervals, calculated by simple Hückel theory, with experimental intervals, the values so obtained are very different from −4·79 eV. This arises primarily because the simple Hückel formalism is based on simple product wave functions and does not directly estimate π-electron interactions, so that it is inadequate for dealing with spectroscopic niceties. For example, according to VESCF calculations the $^1B_{2u}$, $^1B_{1u}$, $^1E_{1u}$, and $^3B_{1u}$ states of benzene are respectively (cf. Pariser 1956*a*) −0·98, −1·24, −1·41, and −0·75 h.u. (Hückel units) above the ground state, while according to simple Hückel calculations all of these states are the same distance, −2 h.u., above the ground state.

charge distribution and energies. When the VESCF matrix elements are considered in this manner (see Table 7) several interesting points emerge.

(i) The Hückel coulomb integrals for the various ring atoms vary in magnitude. This arises from the recognition, in the VESCF method, that the diagonal Hamiltonian matrix element $F_{\mu\mu}$ depends upon the π-electron density on atom μ, P_μ. The corresponding assumption that the Hückel coulomb integral, α_μ^0, is a function of P_μ has occasionally been employed in the past (Laforgue 1949; Wheland and Mann 1949; Pritchard and Sumner 1956). For an alternatant hydrocarbon carbon atom (as in benzene or naphthalene) $F_{\mu\mu}$ has the value $-I_\mu+\frac{1}{2}\gamma_\mu=-6{\cdot}18_7$ eV. The azulene values lie around this figure but, owing to the non-alternant connectivity of azulene, they do not correlate

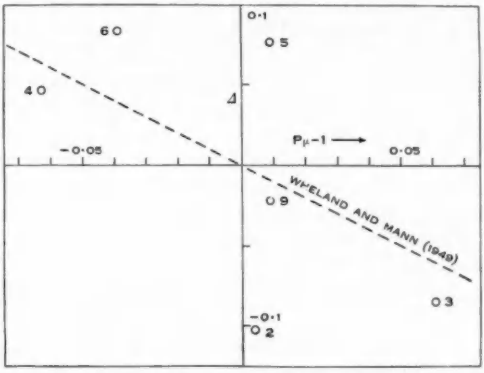

Fig. 1.—Plot of $\Delta=F_{\mu\mu}-1{\cdot}292$ h.u. for the various carbon atoms in azulene. The dashed line represents the functional dependence of coulomb parameter on π-electron density assumed by Wheland and Mann (1949).

monotonically with electron densities (see Fig. 1). Thus the type of dependence of the Hückel coulomb integral upon the electron density assumed by Wheland and Mann, Laforgue, or Pritchard and Sumner is not supported by the VESCF results. The simple type of assumption made by these authors ignores the effects of resonance integral values; the effect of the latter is discussed below.

(ii) The simple Hückel method for a single ring system with all bonds assigned the same value of $\beta_{\mu\nu}^0$ leads directly to the proposition that the atom having the most negative α_μ^0 gains the greatest π-electron density. It follows that α_μ^0 is a useful measure of the electronegativity of atom μ if electronegativity is defined as the ability to gain π-electrons. However, in other than single ring systems the partitioning of the π-electrons among the conjugated atoms is determined not only by the α_μ^0 values but also by the polarizabilities, $\pi_{\mu\mu}$, and, in non-alternant systems it is determined also by values of resonance integrals.*

* As a simple illustration, if in the simple Hückel method the magnitude of the resonance integral of the 9,10 bond in azulene is reduced to zero then the conjugated system is equivalent to that of *cyclo*decapentaene and the π-electron densities all become unity.

TABLE 7

VESCF HAMILTONIAN MATRIX ELEMENTS (METHOD (i)) IN HÜCKEL UNITS

$\beta^0 = -4{\cdot}79$ eV

	(2)									
(2)	1·190	(3)								
(3)	1·001	1·207	(10)							
(10)	—0·006	0·989	1·270	(4)						
(4)	—0·096	0·008	0·967	1·338	(5)					
(5)	0·001	—0·083	—0·010	1·004	1·369	(6)				
(6)	0·052	0·006	—0·111	0·034	0·996	1·375	(7)			
(7)	0·001	0·058	—0·004	—0·120	—0·009	0·996	1·369	(8)		
(8)	—0·096	—0·028	0·125	—0·035	—0·120	0·034	1·004	1·338	(9)	
(9)	—0·006	—0·159	0·501	0·125	—0·004	—0·111	—0·010	0·967	1·270	(1)
(1)	1·001	—0·051	—0·159	—0·028	0·058	0·006	—0·083	0·008	0·989	1·207

When the dependence of α_μ^0 upon P_μ is also included in the calculations the relationship between the final values of the α^0's and the P's is still less direct. For the five-membered ring heterocycles considered in Parts II to IV, when the $F_{\mu\mu}$ differed sufficiently the atom with the most negative value gained the highest π-electron density; but when the $F_{\mu\mu}$ did not differ very greatly then in some cases the relation between $F_{\mu\mu}$ and P_μ was no longer monotonic decreasing. In the case of azulene the other extreme of a monatonic increasing relation between $F_{\mu\mu}$ and P_μ has almost been reached. This shows that one should be cautious in using α_μ^0 as an index of electronegativity. It measures the intensity of the local field at atom μ, but in some types of molecules, of which azulene is an example, special arrangements of other atoms produce π-electron drifts which can swamp the effect of local fields.

(iii) The Hückel resonance integrals of the carbon-carbon bonds all lie in the range $0{\cdot}97\beta^0$ to $1{\cdot}00\beta^0$, apart from that of the 9,10 bond, which has the value $0{\cdot}50\beta^0$. The constancy for the peripheral bonds merely reflects the constancy of bond orders, because the bond lengths, and hence $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$, were taken to be constant, and $F_{\mu\nu}=\beta_{\mu\nu}-\frac{1}{2}P_{\mu\nu}\gamma_{\mu\nu}$. Among the non-neighbour resonance integrals, those which would be appreciable in the absence of the 9,10 linkage (because they involve atoms belonging to opposite " sets " when the alternant starring process (Coulson and Rushbrooke 1940) is applied to *cyclo*decapentaene) still have similar negative values (Hückel units) in azulene. Some others, e.g. F_{49}, with appreciable positive values, must be a consequence of the cross link which is the major " non-alternant " factor in the system.

VIII. Acknowledgment

One of us (M.L.H.) gratefully acknowledges the award of a C.S.I.R.O. studentship.

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THE VARIABLE ELECTRONEGATIVITY METHOD

VII. PYRAZOLE, ITS ANION AND CATION

By R. D. Brown* and M. L. Heffernan*

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Summary

Results of a VESCF treatment of pyrazole, its anion, and cation are reported. A comparison is made of the chemical properties of pyrazole and those predicted from the calculated π-electron densities. An ambiguity in the comparison owing to the rapid tautomerization of pyrazole is emphasized. The calculated π-electron distribution in the anion supports the suggestion made in previous papers that the relative electronegativities of carbon and tertiary nitrogen reverse when their π-electron densities exceed 1·2.

The dipole moment is predicted to be about 2·5 D for pyrazole, in agreement with observations in solution. Theoretical values of ionization potentials are also presented.

An analysis is made of VESCF matrix elements and some empirical guides as to suitable values of coulomb and resonance parameters for five-membered ring nitrogen heterocycles are suggested.

I. Introduction

In previous studies of conjugated molecules by the VESCF method (Brown and Heffernan 1958, 1959*a*, 1959*b*, 1959*c*, 1959*d*, 1959*e*) various aspects of the electronic structures of the molecules have been considered. Three of these are important in the present study of pyrazole, its anion and cation—the problem of electronegativity reversal, the possibility of establishing empirical rules for predicting VESCF matrix elements, and the reliability of dipole moments predicted on the basis of VESCF calculations.

The relationship of the chemical properties of pyrazole to the molecular-orbital calculations also needs to be reconsidered, especially in the light of experimental results obtained since the previous theoretical analysis of the chemistry (Brown 1955).

II. Method

Details of the VESCF method have been given in previous papers of the series (Brown and Heffernan 1958, 1959*a*, 1959*b*, 1959*c*, 1959*d*, 1959*e*) the present study being analogous to that previously reported for glyoxaline (Part IV). There being no accurate experimental observations on the geometry of pyrazole, the pyrrole geometry was adopted. This meant that some of the basic integrals

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computed for pyrrole (Part II) could be used in the present calculations. Values of some penetration integrals not previously published were obtained by short graphical interpolations; those involving the two nitrogens were directly evaluated from tables of basic integrals. Since method AP was used, penetrations of orbitals into position 1 correspond to penetration into N^+ and thus such integrals have considerably larger values than do neutral atom penetrations. Values of penetration integrals not previously listed are given in Table 1.

TABLE 1

INTERPOLATED VALUES OF PENETRATION INTEGRALS (ev)

	Integral	r (A)	Value	Integral	r (A)	Value
Pyrazole	(2 : 33)	1·371	1·51	(5 : 22)	2·251	$0·00_3$
	(3 : 22)	1·371	0·71	(2 : 55)	2·251	0·49
	(1 : 22)	1·383	10·017*	(2 : 44)	2·258	0·49
	(2 : 11)	1·383	1·547*	(4 : 22)	2·258	$0·00_3$
Pyrazole anion	(3 : 44)	1·429	0·569*	(1 : 22)	1·383	1·547*
	(2 : 44)	2·30	0·40	(5 : 22)	2·26	$0·00_3$
	(2 : 33)	1·371	1·51	(4 : 22)	2·30	$0·00_2$
	(1 : 33)	2·26	0·49	(3 : 22)	1·371	0·71
	(5 : 33)	2·22	0·02			
Pyrazole cation	(3 : 44)	1·429	0·569	(1 : 22)	1·383	10·017
	(2 : 44)	2·30	6·25	(5 : 22)	2·26	$0·00_3$
	(2 : 33)	1·371	9·965	(4 : 22)	2·30	$0·00_2$
	(1 : 33)	2·26	6·26	(3 : 22)	1·371	0·71
	(5 : 33)	2·22	0·02			

* These values were calculated directly from tables of molecular integrals.

Values used for core resonance integrals were: $\beta_{CN} = -2·30$ eV; $\beta_{34} = -1·905$ eV; $\beta_{45} = -2·650$ eV; $\beta_{NN} = -2·35$ eV, the two carbon nitrogen bonds being assigned the same value for their core resonance integrals. The first three values were those used in pyrrole, while the β_{NN} value is that found by Paoloni (1956) in a Pariser-Parr treatment of *s*-tetrazine.

TABLE 2

ASSUMED GEOMETRY FOR PYRAZOLE ANION AND CATION

N_1–N_2	1·383 A	N_1–C_5	2·26 A
N_2–C_3	1·371	N_1–C_4	2·30
C_3–C_4	1·429	C_5–C_5	2·22

For the anion and cation the geometry summarized in Table 2 was adopted. Penetration integrals not previously listed are included in Table 1. The core resonance integrals were assigned the same values as listed above for pyrazole itself except that a value of −1·905 eV was used for β_{45} to give the core field the same symmetry as the cation and anion.

TABLE 3

VALUES* OF VESCF QUANTITIES FOR PYRAZOLE

Energies in eV

Quantity	Method		Quantity	Method	
	AP	BP		AP	BP
Z_1	4·022	4·020	F_{11}	—15·275	—12·180
Z_2	3·851	3·835	F_{22}	—10·405	—7·591
Z_3	3·235	3·244	F_{33}	—8·915	—5·699
Z_4	3·246	3·224	F_{44}	—8·667	—5·864
Z_5	3·197	3·227	F_{55}	—10·402	—6·538
I_1	25·726	25·703	F_{12}	—4·236	—4·156
I_2	13·462	13·246	F_{23}	—5·405	—5·407
I_3	11·365	11·465	F_{34}	—3·800	—3·791
I_4	11·497	11·246	F_{45}	—5·629	—5·637
I_5	10·932	11·274	F_{51}	—4·124	—4·206
α_1	—56·489	—53·331	P_1	1·654	1·658
α_2	—51·786	—48·924	P_2	1·140	1·184
α_3	—46·991	—43·987	P_3	1·044	1·018
α_4	—46·551	—43·510	P_4	1·010	1·073
α_5	—49·352	—45·698	P_5	1·151	1·066

* Z_μ and P_μ are pure numbers.

Final values of the VESCF quantities are listed in Tables 3 and 4. For the pyrazole anion and cation the core coulomb integrals, α_μ, obtained separately by methods AP and BP, were averaged and the resultant mean values used in the VESCF iterations.

TABLE 4

VALUES* OF VESCF QUANTITIES FOR PYRAZOLE ANION AND CATION†

Energies in eV

Quantity	Anion	Cation	Quantity	Anion	Cation
Z_2	3·826	4·034	F_{22}	—1·164	—21·575
Z_3	3·183	3·280	F_{33}	—0·748	—15·025
Z_4	3·181	3·272	F_{44}	—0·519	—13·741
I_2	13·119	25·909	F_{12}	—4·924	—3·696
I_3	10·779	11·887	F_{23}	—4·841	—4·575
I_4	10·750	11·786	F_{34}	—4·255	—4·400
α_2	—41·858	—63·392	P_2	1·210	1·618
α_3	—39·036	—54·052	P_3	1·190	0·913
α_4	—38·353	—51·115	P_4	1·199	0·936

* Z_μ and P_μ are pure numbers.

† Average of values by methods AP and BP.

III. π-Electron Densities and Chemical Reactivities

The resultant π-electron densities for the three carbon atoms in pyrazole (average of results by methods AP and BP,* see Fig. 1) all exceed unity, in conformity with the relatively high susceptibility to attack by electrophils shown by pyrazole. Experimentally the 4-position is found to be preferentially attacked under all conditions. Nitration (Buchner and Fritsch 1893; Knorr 1894; Hüttel, Büchele, and Jochum 1955) and sulphonation (Knorr 1894) occur at this position in strongly acidic media; halogenation in inert (Hüttel, Wagner, and Jochum 1955; Hüttel, Schäfer, and Welzel 1956) or neutral aqueous (Hüttel, Schäfer, and Jochum 1955) solvents also involves this position. The interpretation of these observations is more ambiguous than was the case for glyoxaline (Part IV) because the mechanisms of the reactions are uncertain, especially with regard to the state of protonation of the heterocyclic ring. It seems very likely that in strongly acidic media the cation is involved, at least in the case of nitration, because Hüttel and Büchele (1955) found that in acetic anhydride the stable *N*-nitrocompound forms, this presumably happening unless both nitrogens are protonated.

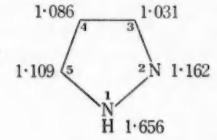

Fig. 1

If the cation is involved, the orientation might be expected to correlate with electrophilic localization energies rather than π-electron densities (Brown 1958; Brown and Coller 1959; Brown and Harcourt 1959). Localization energies have not been calculated for the cation by the VESCF method but the relative values of these are not likely to be very different from those found by the simple Hückel method. The latter (Brown 1955) strongly favour the 4-position.

The halogenations in aqueous media might involve either the anion or the free base. If the anion is involved, the preferential attack of the 4-position is understandable from the relative values of the π-electron densities (Table 4), but those of the free base (Fig. 1 and Table 3) do not unambiguously predict such an orientation. The halogenations in carbon tetrachloride presumably occur by electrophilic substitution in the free base by halogen molecules. It would thus seem that the chemical properties probably do require the π-electron density to be greatest at the 4-position; if so then the simple average of the results by methods AP and BP is not completely satisfactory—more weight should be allotted to method BP.

However, a further complication arises. The tautomeric exchange of a proton between the two nitrogens undoubtedly occurs far more rapidly than does any electrophilic substitution. The attacking electrophil thus "sees" some average charge distribution in the case of positions 3 and 5. Furthermore, neither nitrogen will, on the average, be fully protonated. Thus it cannot be claimed with full confidence that the charge distribution shown in Figure 1

* The significance of the labels AP and BP is fully set out in Part V. It may be noted that the calculations described in Parts II–IV used method *P* exclusively for selecting values of coulomb repulsion integrals so that the labels *A*, *B*, and *C* used in those papers are, in terms of the expanded notation of Part IV, AP, BP, and CP.

is incorrect. This is unfortunate because we are seeking crucial tests for calculated π-electron densities to determine the most appropriate treatment of penetration integrals (i.e. to decide the relative merits of methods A and B).

For any of the reactions which might occur in the anion this ambiguity connected with "tautomeric averaging" no longer arises. The calculated π-electron densities for the anion imply that the five-ring atoms have virtually identical electronegativities with respect to π-electrons. This further supports the conclusion reached in previous studies (Brown and Heffernan 1959*b*, 1959*c*) that electronegativity reversal for C and N (both of core charge +1) will occur when their π-electron densities exceed a value of about 1·2.

IV. Dipole Moment

The π-electron densities obtained by methods AP and BP for pyrazole (Table 3) have been used to estimate the dipole moment (Table 5). The results compare very favourably with the observed moment (Jacobs 1957) of *N*-methylpyrazole (2·28 D in benzene), it being borne in mind that solution values generally have to be increased by 10 per cent. or so to agree with vapour phase values.

Table 5

DIPOLE MOMENT OF PYRAZOLE (D)

Quantity	Method AP		Method BP	
	*X**	*Y**	*X**	*Y**
π-Moment	1·667	0·058	1·892	0·453
N-Hybridization ..	—0·602	1·807	—0·607	1·814
H-Hybridization ..	—0·077	0·183	—0·077	0·183
Total	0·998	2·048	1·208	2·450
Resultant	2·28		2·73	

* Components in *X*- and *Y*-directions; *X*-direction is along the N—H bond, the *Y*-direction perpendicular to this and in the molecular plane.

The measured moment of pyrazole itself (Jacobs 1957) is complicated by association through hydrogen bonding, so that a low value (1·57 D) was found in benzene, although in dioxane, where solute association is probably largely replaced by solvation, a higher value (2·2 D) was found.

The present calculations lead to both a magnitude and a direction for the molecular dipole moment vector. It is to be hoped that in due course an experimental value for the direction of the vector in the molecule will become available from microwave spectral studies on pyrazole.

V. Ionization Potentials

The first two π-electron ionization potentials of pyrazole, calculated by the VESCF procedure, are given in Table 6, with corresponding values for related molecules for comparison. The experimental values are known for benzene

(9·24 eV) and pyrrole (8·90 eV). The present study implies that the first ionization potential of pyrazole will be about 9 eV, rather higher than the pyrrole value, and perhaps not quite as high as the benzene value.

The nitrogen n-electron ionization potential, obtained simply from the nitrogen π-electron density as outlined in previous papers (Brown and Heffernan 1958, 1959*b*, 1959*c*), is calculated to be about 14·2 eV. From comparison with the data in Table 6 the lowest ionization potential is clearly predicted to be a π-electron potential.

TABLE 6

CALCULATED IONIZATION POTENTIALS (ev)

Molecule	Method AP		Method BP	
	1st	2nd	1st	2nd
Pyrazole ..	14·68	14·82	11·53	11·66
Pyrrole ..	14·13	14·33	11·27	11·62
Glyoxaline	14·51	15·02	11·10	12·03
Benzene ..	14·64	14·64	12·66	12·66

VI. PARAMETERS FOR THE HÜCKEL MO METHOD

The VESCF Hamiltonian matrix elements derived in the present calculations provide further data from which to seek empirical rules for predicting matrix elements. A detailed discussion of previous results has been given in Part IV. In the previous discussion coulomb and auxiliary inductive parameters, h and h', were found to have values in the ranges $h=0·08$–$0·10$, $h'=0·03$–$0·07$ for tertiary nitrogen, $h=1·31$–$1·54$, $h'=0·25$–$0·34$ for secondary nitrogen, these parameters showing an approximate, inverse correlation with the π-electron densities on the nitrogen. Resonance parameters for nearest neighbours showed a close correlation with the corresponding bond lengths. For non-neighbour atom pairs, negative values of resonance parameters were found, falling into two main

TABLE 7

VESCF HAMILTONIAN MATRIX ELEMENTS

Hückel units

$\mu\nu$*	Pyrazole†	Anion	Cation	$\mu\nu$*	Pyrazole†	Anion	Cation
11	2·87	0·24	4·50	45	1·18	0·89	0·92
22	1·88	0·24	4·50	51	0·87	1·01	0·96
33	1·53	0·16	3·14	13	—0·18	—0·15	—0·23
44	1·52	0·11	2·87	14	—0·16	—0·15	—0·10
55	1·77	0·16	3·14	24	—0·05	—0·15	—0·10
12	0·88	1·03	0·77	25	—0·21	—0·15	—0·23
23	1·13	1·01	0·96	35	—0·04	—0·15	0·12
34	0·79	0·89	0·92				

* Subscripts of $F_{\mu\nu}$.

† Mean of values by methods AP and BP.

groups, one around −0·17 and another around −0·05. The data in Table 7 are a supplement to Table 9 of Part IV, giving values of matrix elements in Hückel units (1 h.u. = −4·79 eV). It is convenient to consider coulomb and resonance parameters separately.

Coulomb Parameters.—When the 4-position, which is well-removed from the heteroatoms, is used as origin, the values found for the coulomb parameter, h, and auxiliary inductive parameter, h', of the heteroatoms are:

Secondary nitrogen: h = 1·35 (pyrazole), 1·63 (cation)
h' = 0·25 (pyrazole), 0·27 (cation)

Tertiary nitrogen: h = 0·13 (anion)
h' = 0·01 (anion).

The inverse relationship between h and π-electron density, mentioned in Part IV, becomes less definite in the light of the additional data. Plots of h_μ against P_μ for all data so far obtained for both secondary and tertiary nitrogen are shown in Figures 2 and 3. Little overall correlation between the two variables is evident. For tertiary nitrogen h is close to 0·1 regardless of P_μ for five-membered ring systems, the pyridine value however being appreciably greater. For secondary nitrogens, h is near 1·35 in uncharged systems but in the cations larger values emerge. For nitrogens in uncharged five-membered ring compounds the following parameters are therefore tentatively suggested:

Secondary nitrogen: h = 1·35, h' = 0·25
Tertiary nitrogen: h = 0·1, h' = 0·02

but considerable variations from these values must be admitted, particularly in charged systems. It should also be borne in mind that these values are appropriate only when non-neighbour interactions are included and that they are therefore not apposite for the simple Hückel approximation in which such interactions are ignored.

The lack of correlation of coulomb parameters with π-electron densities is not surprising, for reasons outlined when considering the VESCF results for azulene (Part VI). When non-zero values for non-neighbour resonance integrals enter into the calculations (see below) all heterosystems are non-alternant and in such cases the charge distribution is partly determined by the values of the resonance integrals.

Resonance Parameters.—For nearest neighbours the resonance parameters do not deviate greatly from unity and in general reflect the geometrical assumptions made at the outset. Until "geometrically self-consistent" calculations are done (i.e. calculations in which bond lengths are estimated from calculated bond orders and iterations continued until self-consistent results emerge) there seems little point in analysing the values in detail.

For non-neighbours the resonance parameters follow the same pattern as that previously recorded for other five-membered ring nitrogen compounds. In the anion the values are indistinguishable from the *cyclo*pentadienyl anion value (−0·15 h.u.), a further indication that the five conjugated atoms are

virtually indistinguishable from the point of view of the π-electrons in the pyrazole anion. For the free base, as in previous cases, two sets of values, near −0·17 and −0·05 h.u. respectively, are found, while a still greater variation in values, including one with a positive sign, occur for the cation.

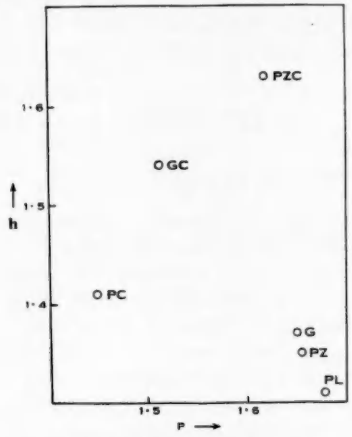

Fig. 2.—Relation between coulomb parameter and π-electron density for secondary nitrogen.

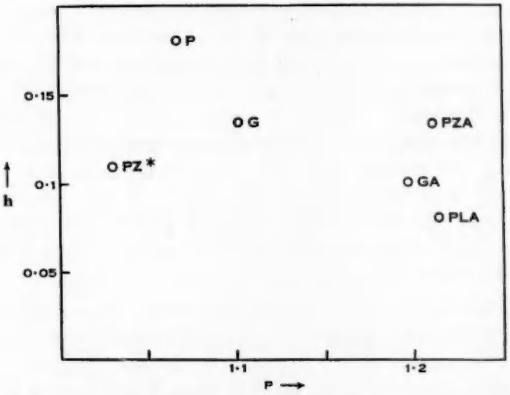

Fig. 3.—Relation between coulomb parameter and π-electron density for tertiary nitrogen.

Some semblance of a pattern for these values is beginning to appear. The values around −0·05 h.u. involve the 2,4 and 3,5 interactions for all free bases so far studied—pyrrole, glyoxaline, and pyrazole—and thus appear to be confined to interactions involving either one of the two positions adjacent to nitrogen

of core charge +2. In the cations, however (of glyoxaline and pyrazole), the least negative values occur for the next-to-nearest-neighbour interactions involving either one of the nitrogens. It seems likely that further studies of five-membered ring heterocycles, such as furan and indole, may result in fairly clear-cut rules for predicting the values of these matrix elements.

VII. Acknowledgment

One of us (M.L.H.) gratefully acknowledges the award of a C.S.I.R.O. studentship.

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THE EXTRACTION OF CERTAIN CATIONS FROM AQUEOUS SOLUTION WITH DI-(2-ETHYLHEXYL)ORTHOPHOSPHATE

By D. C. MADIGAN*

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Summary

Equations derived from experimental data are presented for the distribution of divalent copper, cobalt, and nickel between aqueous sulphate solution and solution of di-(2-ethylhexyl)orthophosphate (EHPA) in kerosene. These equations approach, though they are not identical with, the distribution equation derived from a simple extraction theory. The same theory cannot be applied to the extraction of sodium. The marked difference in behaviour between the alkali and transition metals is explained in terms of the different structures of their compounds with EHPA.

I. INTRODUCTION

The use of alkyl phosphates, and particularly of di-(2-ethylhexyl)orthophosphate (EHPA), for the extraction of uranium from aqueous solutions is well known (Blake, Baes, and Brown 1958). The alkyl phosphate, dissolved in a suitable diluent, normally kerosene, is contacted with the liquor obtained by leaching uranium ores with sulphuric acid. Uranium passes from the aqueous to the organic phase, from which it may be recovered by stripping with various reagents, such as hydrochloric acid or sodium carbonate solutions. If sodium carbonate is used to strip kerosene solutions of EHPA, it is necessary to modify the organic phase by the addition of small quantities of certain neutral organophosphorus compounds, such as tributyl phosphate, or of long-chain alcohols, such as 2-ethylhexanol. The modifier prevents the formation of a third liquid phase, containing the sodium compound of EHPA, which would separate in its absence. The use of alkyl phosphates for the extraction of thorium has also been reported (Madigan 1959).

The present investigation of the extraction process was undertaken as part of a study of the separation of base metals by solvent extraction, with special reference to copper, cobalt, and nickel.

II. THEORY

A solution of EHPA in an organic solvent is thoroughly mixed with an aqueous solution containing a cation M^{n+} until equilibrium is attained. EHPA is represented by HA, where $A=(C_8H_{17})_2PO_4$. A process in four stages is postulated for the extraction of the cation, as follows:

(i) Distribution of EHPA between the organic and aqueous phases, according to the equation

$$(HA)_o \rightleftharpoons (HA)_w, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where the subscripts o and w denote the organic and aqueous phases respectively.

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This is described by the distribution constant k_1, given by

$$\frac{(a_{\overline{\mathrm{HA}}})_w}{(a_{\mathrm{HA}})_o}=k_1, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where a denotes activity.

(ii) Dissociation of EHPA in the aqueous phase

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}'. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

This is described by the dissociation constant k_2, given by

$$\left(\frac{a_{\mathrm{A}'} \cdot a_{\mathrm{H}^+}}{a_{\mathrm{HA}}}\right)_w = k_2. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

(iii) Formation of metal compound in the aqueous phase

$$\mathrm{M}^{n+} + n\mathrm{A}' \rightleftharpoons \mathrm{MA}_n. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

This is described by the formation constant k_3, given by

$$\left(\frac{a_{\mathrm{MA}_n}}{a_{\mathrm{M}^{n+}} \cdot a_{\mathrm{A}'}^n}\right)_w = k_3. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

(iv) Distribution of metal compound between the aqueous and organic phases

$$(\mathrm{MA}_n)_w \rightleftharpoons (\mathrm{MA}_n)_o. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

This is described by the distribution constant k_4, given by

$$\frac{(a_{\mathrm{MA}_n})_o}{(a_{\mathrm{MA}_n})_w}=k_4. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

The distribution ratio D of a metal between the two phases is defined as

$$D=\frac{\text{concentration of metal in organic phase}}{\text{concentration of metal in aqueous phase}}. \quad \ldots\ldots \quad (9)$$

If it is assumed that all the metal in the organic phase is present as the compound MA_n, and all the metal in the aqueous phase as metal ions M^{n+}, then it follows from (2), (4), (6), and (8) that

$$D=k_1^n k_2^n k_3 k_4 \frac{(a_{\mathrm{HA}}^n)_o}{(a_{\mathrm{H}^+}^n)_w} \times \frac{(y_{\mathrm{M}^{n+}})_w}{(y_{\mathrm{MA}_n})_o}, \quad \ldots\ldots\ldots\ldots \quad (10)$$

where y denotes molar activity coefficient.

At constant temperature k_1 is determined by the solvent system, and k_3 and k_4 are determined by the cation. If the pH of the aqueous phase may be taken as a measure of the hydrogen ion activity, (10) becomes, for a given solvent system and a given cation,

$$D=K(c_{\mathrm{HA}}^n)_o \cdot 10^{n.\mathrm{pH}} \cdot (y_{\mathrm{M}^{n+}})_w \cdot (y_{\mathrm{HA}}^n/y_{\mathrm{MA}_n})_o, \quad \ldots\ldots \quad (11)$$

where c denotes molarity and $K=k_1^n k_2^n k_3 k_4$ is an extraction constant determined only by the temperature.

If the solutions are sufficiently dilute for the activity coefficients of the species in the organic phase to be equal to unity, (11) reduces to

$$D=K(c_{HA}^n)_o \cdot 10^{n.pH} \cdot (y_{M^{n+}})_w, \quad \ldots\ldots\ldots\ldots \quad (12)$$

and by taking logarithms

$$\log D=n[\mathrm{pH}+\log (c_{HA})_o \cdot (y_{M^{n+}}^{1/n})_w]+\log K. \quad \ldots\ldots \quad (13)$$

Experimental work was undertaken to test the validity of this equation.

III. Experimental

A 0·05M solution of EHPA in kerosene, containing 2-ethylhexanol (20 ml/l), was stirred with various aqueous sulphate solutions. A phase ratio of 1·0, a temperature of 26·0 °C, and a contact time of 2 hr were used throughout the experiments. After contact the phases were separated and analysed. Both organic and aqueous phases were prepared for analysis by evaporation, followed

Table 1

Extraction of copper, cobalt, and nickel with EHPA: analysis of equilibrium phases

Millimoles/litre

No.	Aqueous Phase					Organic Phase				Distribution Ratio (D)
	pH	M*	Na	SO_4	P	M*	Na	P	Free EHPA	
Copper										
1	5·00	0·472	50·4	25·5	0·324	18·6	0·70	48·4	10·5	39·4
2	4·05	5·51	51·3	31·1	0·056	13·4	0·43	48·4	21·2	2·43
3	3·78	8·18	50·9	33·6	0·056	10·5	0·57	48·7	27·1	1·28
4	3·50	11·5	51·7	37·3	0·042	7·24	0·78	48·6	33·3	0·630
5	3·30	14·3	52·2	40·4	0·028	4·25	0·39	48·3	39·4	0·297
6	3·00	16·7	51·7	42·6	0·042	2·20	0·35	48·7	44·0	0·132
Cobalt										
1	5·72	2·21	48·7	26·1	0·93	18·7	1·22	47·4	8·78	8·46
2	4·54	11·4	49·6	36·0	0·32	9·33	0·70	47·7	28·3	0·819
3	4·34	13·9	50·0	38·8	0·21	6·79	0·61	48·0	33·8	0·489
4	4·00	16·8	51·5	42·5	0·085	3·23	0·30	48·0	41·2	0·192
5	3·34	20·0	49·6	44·7	0·14	0·48	0·39	48·1	46·8	0·024
6	2·60	20·2	51·8	46·0	0·07	0·051	0·00	48·7	48·6	0·00252
Nickel										
1	5·70	2·21	49·6	26·5	0·92	17·6	2·35	47·7	10·2	7·96
2	5·05	6·64	50·4	31·6	0·38	13·1	1·26	48·6	21·0	1·97
3	4·80	9·54	51·3	35·0	0·32	10·2	1·00	48·4	27·0	1·07
4	4·50	13·0	50·9	38·3	0·24	6·82	0·74	48·3	33·9	0·525
5	4·22	15·8	50·9	41·2	0·15	3·58	0·61	48·7	40·9	0·227
6	3·70	18·7	51·3	44·3	0·11	0·68	0·39	48·4	46·7	0·0364

* M=Cu, Co, or Ni.

by digestion of the residue with nitric and perchloric acids. Copper, cobalt, and nickel were determined colorimetrically using 2,2′-diquinolyl, nitroso R salt, and dimethyl glyoxime (after oxidation of the nickel with iodine) respectively. Sodium was determined by flame photometry. Phosphorus was determined colorimetrically by the vanadate–molybdate method and sulphate was determined gravimetrically. The phosphorus in the organic phase was taken as a measure of the total EHPA present, and the free EHPA was obtained by difference.

TABLE 2

EXTRACTION OF SODIUM WITH EHPA : ANALYSIS OF EQUILIBRIUM PHASES

Millimoles/litre

No.	Aqueous Phase				Organic Phase		Distribution Ratio (D)
	pH	Na Salt of EHPA	NaOH	Na_2SO_4	Na Salt of EHPA	Free EHPA	
1	6·40	27·7	0·1	Nil	3·35	21·1	0·121
2	6·65	38·2	0·5	„	1·83	9·72	0·0473
3	8·40	46·6	3·8	„	0·65	1·60	0·0129
4	11·55	47·2	11·9	„	0·57	1·40	0·00964
5	12·10	47·0	28·2	„	0·61	1·64	0·00811
6	>13	46·1	50·4	„	1·09	1·59	0·0113
1	5·51	2·53	Nil	101	9·57	37·3	0·0468
2	5·74	3·10	„	101	18·0	29·0	0·0878
3	5·90	3·38	„	101	28·3	17·9	0·138
4	6·22	3·52	„	101	38·3	7·7	0·186
5	8·31	3·62	„	101	46·1	Nil	0·224
6	11·48	3·53	4·4	103	46·1	„	0·216

(*a*) *Extraction of Copper, Cobalt, and Nickel*

The aqueous phases before contact consisted of solutions of Cu(II), Co(II), and Ni(II) sulphates acidified with varying amounts of sulphuric acid. The EHPA solution before being brought into contact with these solutions was converted to the sodium form by shaking with an equal volume of M Na_2CO_3 solution. The composition of the equilibrium phases, in millimoles per litre (except pH), is shown in Table 1. It was found that if the metals were precipitated from their aqueous solutions as hydroxides or carbonates by the addition of alkali, the precipitate could be readily extracted by EHPA solution, provided that there was not too large an excess of alkali present. A volume of 0·1M Na_2CO_3 solution was added to an equal volume of 0·1M $CoSO_4$ solution and the precipitated cobalt was readily extracted by EHPA. When the concentration of Na_2CO_3 was increased to 0·2M, extraction of cobalt still took place, but when it was increased to 1·0M there was no extraction. Similar results were obtained when NaOH was substituted for Na_2CO_3. Extraction of metal from the precipitated carbonate was accompanied by the evolution of CO_2.

(*b*) *Extraction of Sodium*

The aqueous phases before contact consisted of solutions of NaOH alone, and solutions of NaOH containing Na_2SO_4/(100 mM/l). When the organic and aqueous phases were mixed together emulsification occurred in the absence of Na_2SO_4, and it was necessary to centrifuge the mixture to obtain satisfactory phase separation. The composition of the equilibrium phases is shown in Table 2.

IV. Discussion

(*a*) *Control of pH*

Extraction of metal ions from aqueous solutions by solutions of free EHPA in organic solvents involves the transfer of an equivalent quantity of hydrogen ions to the aqueous phase. The overall reaction may be represented by the equation

$$n\overline{R_2HPO_4}+M^{n+}=\overline{M(R_2PO_4)_n}+nH^+, \quad \ldots\ldots\ldots \quad (14)$$

where R=2-ethylhexyl. To achieve appreciable transfer of metal to the organic phase it is generally necessary to remove hydrogen ions from the aqueous phase, so that reaction (**14**) may proceed to the right. This may be done by the addition of alkali (e.g. NaOH or Na_2CO_3) to the aqueous phase, which causes precipitation of the metal, but the precipitate is readily extracted provided an excess of alkali is avoided. If hydroxide is used and the metal is divalent, the reactions taking place in the aqueous phase may be represented by

$$2\overline{R_2HPO_4}=2\overline{R_2PO_4'}+2H^+, \quad \ldots\ldots\ldots\ldots\ldots \quad (15)$$

$$M(OH)_2=M^{2+}+2OH', \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

$$2OH'+2H^+=2H_2O, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (17)$$

$$2\overline{R_2PO_4'}+M^{2+}=\overline{M(R_2PO_4)_2}. \quad \ldots\ldots\ldots\ldots\ldots \quad (18)$$

If carbonate is used, a similar set of reactions may be postulated. The presence of a large excess of alkali would suppress the ionization represented by equation (**16**), and so the failure to extract the metal under this condition may be accounted for.

Instead of adding alkali to the aqueous phase, the EHPA solution may itself be contacted with alkali to convert the EHPA to the sodium compound. The final pH of the equilibrium aqueous phase may then be easily controlled by adjusting the acidity of the solution before contact, and this was the method adopted in the experimental work. In order to prevent the formation of a separate liquid phase containing the sodium compound of EHPA, 2-ethylhexanol was added to the EHPA solution. The following reactions may be postulated :

(i) Distribution of the sodium compound between the organic and aqueous phases.

(ii) Dissociation of the sodium compound in the aqueous phase to yield A′ ions.

(iii) Formation of EHPA in the aqueous phase $A'+H^+ \rightleftharpoons HA$.

(iv) Formation of the heavy metal compound in the aqueous phase.
(v) Distribution of EHPA between the aqueous and organic phases.
(vi) Distribution of the heavy metal compound between the aqueous and organic phases.

Reactions (iii) to (vi) are described by the constants k_2, k_3, k_1, and k_4 respectively, and from these equation (**10**) is derived without reference to the equilibria involved in (i) and (ii). The final result then should be the same as if the alkali had been added to the aqueous phase before contact, and this has been confirmed by experiment. Of course any sodium present in the organic phase at equilibrium must be allowed for in calculating the free EHPA.

(*b*) *Contact Time*

A contact time of 2 hr was allowed in each case, but equilibrium was reached much more rapidly than this. In the extraction of Cu(II), Co(II), and Ni(II) no significant difference was found between a contact time of 10 min and of 2 hr.

(*c*) *Extraction of Cu(II), Co(II), and Ni(II)*

If the distribution ratio is correctly given by equation (**13**), a plot of log D against pH + log $(c_{\mathrm{EHPA}})_o(y^{\frac{1}{2}}_{\mathrm{M}^{2+}})_w$ should give a straight line of slope 2. A plot of these functions is shown in Figure 1. The activity coefficient y of the metal ion in the aqueous phase was calculated from the Debye-Hückel equation in the form

$$\log y_i = -[A z_i^2 \sqrt{\mu}/(1+\sqrt{\mu})],$$

in which y_i is the molar activity coefficient and Z_i the charge of the ion i, and μ is the molar ionic strength of the solution.

In each case the points lie on a straight line, but the slope, instead of being 2, is 1·73 for Cu(II), 1·45 for Co(II), and 1·68 for Ni(II). This divergence from the theoretical slope may be due to several causes, and does not necessarily invalidate the postulated four-stage extraction process described above. Equation (**13**) involves the assumption that the ratio $(y_{\mathrm{EHPA}}/y^{1/n}_{\mathrm{M(EHPA)}n})_o$ is unity. This may not be so, and deviations from unity could account for the difference in slope. Equation (**13**) also involves the assumption that all the metal in the aqueous phase is present in the form of metal ions M^{n+}, whereas appreciable amounts of sulphato complexes, such as $\mathrm{M(SO_4)_2^{"}}$, may be present. Further, hydrolysis of the metal ion may occur, for example,

$$\mathrm{M}^{n+} + \mathrm{H_2O} = \mathrm{MOH}^{(n-1)+} + \mathrm{H}^+.$$

Since hydrolysis will increase as the pH is raised, owing to the removal of the hydrogen ion, equation (**13**) can only be expected to hold at pH values sufficiently low for hydrolysis of the metal ion to be negligible.

There are other sources of error that are likely to be of less significance than those already mentioned. One is the approximate value of the activity coefficients calculated from the Debye-Hückel equation. Errors due to this cause alone could not however account for the observed results, since to obtain the predicted slope of 2 it would be necessary for the activity coefficients of the metal

ions in the aqueous phase to increase with the ionic strength. This can scarcely be considered possible within the range of concentrations used. Again, the assumption that pH may be taken as a measure of hydrogen ion activity may involve some error, though this is unlikely to be significant in dilute solutions of simple electrolytes.

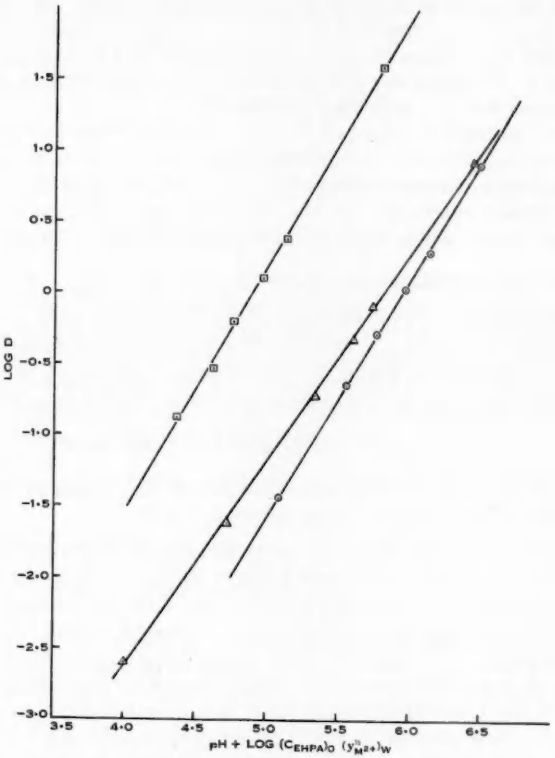


Fig. 1.—Extraction of Cu, Co, and Ni with EHPA.
□ Cu; △ Co; ○ Ni.

(*d*) *Empirical Equations*

A plot of log D against pH+log $(c_{EHPA})_o$ also gave a straight line in each case, leading to empirical equations as follows:

$$\text{for Cu(II)},\ \log D = 1{\cdot}82[\text{pH} + \log (c_{EHPA})_o] - 9{\cdot}36, \quad \ldots\ (19)$$
$$\text{for Co(II)},\ \log D = 1{\cdot}55[\text{pH} + \log (c_{EHPA})_o] - 9{\cdot}39, \quad \ldots\ (20)$$
$$\text{for Ni(II)},\ \log D = 1{\cdot}74[\text{pH} + \log (c_{EHPA})_o] - 10{\cdot}78, \quad \ldots\ (21)$$

where $(c_{EHPA})_o$, the concentration of free EHPA in the organic phase, is expressed in millimoles per litre.

The relation between the distribution ratio D and the percentage of metal extracted into the organic phase, E, is given by

$$E = \frac{100D}{D+(V_w/V_o)}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (22)$$

in which V_w is the volume of the aqueous phase and V_o the volume of the organic phase. If the phase ratio V_w/V_o is fixed and if a value is assigned to $(c_{EHPA})_o$, the fraction of metal that can be extracted at any value of the pH of the aqueous phase may be calculated from equations (19)–(22). Extraction curves so calculated, for a phase ratio of 1 and a concentration of free EHPA in the organic phase of 10 mM/l are shown in Figure 2.

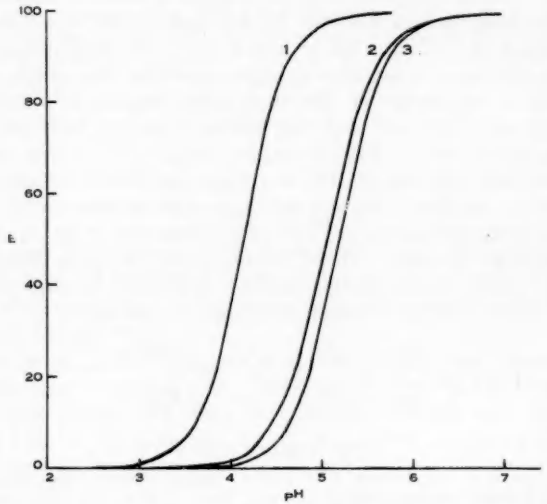


Fig. 2.—Extraction of Cu, Co, and Ni with EHPA; phase ratio = 1; $(c_{EHPA})_o = 10$ mM. 1, Cu; 2, Co; 3, Ni.

(e) *Extraction of Sodium*

If equation (13) is applicable to the extraction of sodium, a plot of log D against pH + log $(EHPA)_o(y_{Na^+})_w$ should give a straight line of unit slope. The points, however, obtained by plotting these functions do not lie on a straight line, and in fact the extraction of sodium bears no relation whatever to equation (13).

The sodium compound of EHPA is a soft waxy material that dissolves or disperses in water to form a turbid solution, from which it is salted out by the addition of NaCl, Na_2SO_4, or Na_2CO_3. The solution forms a stable froth on shaking, and has the power of emulsifying oils. If a kerosene solution of EHPA is shaken with an aqueous solution of NaOH, most of the EHPA passes into the aqueous phase and considerable emulsification takes place. If sodium salts

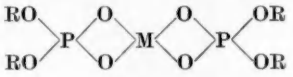
are added the emulsion is broken and the sodium compound of EHPA separates as a liquid phase, which also contains some kerosene and water. As already remarked, this phase can be incorporated in the kerosene phase by the addition of suitable modifiers.

The potassium and ammonium compounds of EHPA were found to have properties very similar to those of the sodium compound.

(*f*) *Conclusions*

It is clear that the alkali metal compounds of EHPA are very similar to the soaps; they form colloidal solutions in water, in which, by analogy with the soaps, ionic and molecular association and micelle formation may be supposed to take place. Association may also occur in the organic phase. The extraction theory presented in Section II of the present paper is based on equilibria between simple unassociated molecular species in each phase, and so cannot be applied to the extraction of sodium or other metals that form soap-like colloidal compounds with EHPA. To derive extraction equations for metals of this type would require a knowledge of the complicated equilibria existing between individual ions and molecules and the various ionic and molecular aggregates and micelles.

The extraction of Cu(II), Co(II), and Ni(II), on the other hand, approaches that predicted by equation (**13**), and the compounds of these metals with EHPA exhibit no soap-like properties, are virtually insoluble in water, and are readily soluble in organic solvents. These facts suggest that the transition metal compounds of EHPA are not simple salts but coordination compounds in which the chelated metal atom is surrounded by organic radicles:



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OBSERVATIONS ON THE SYSTEMS Th–S, Th–Se, AND Th–Te

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Summary

A reinvestigation of these systems has indicated the marked effect of the purity of materials on the phases formed. New polychalcogenides have been found ($ThS_{2\cdot5}$ and $ThSe_{2\cdot5}$ having tetragonal symmetry, and $ThTe_3$ monoclinic), as also has a sesquitelluride (Th_2Te_3, with hexagonal symmetry) which is probably non-stoichiometric. Discrepancies between the present results and those of previous workers are discussed.

I. Introduction

The previous work in these systems is summarized in Table 1 and the following :

(*a*) *Th-S System*

Strotzer and Zumbusch (1941) synthesized Th-S compounds by heating the elements in sealed evacuated tubes for up to 150 hr at 600–900 °C. They used tensiometric analysis, X-ray diffraction, and density determinations in their study of the materials.

Eastman *et al.* (1950) reinvestigated the system some years later; the thorium metal used contained a high proportion of oxygen but all samples were analysed. Their compounds were prepared in various ways from thorium hydride and H_2S, or ThO_2, carbon, and H_2S. X-Ray crystallographic data for the phases prepared by these workers are due to Zachariasen (1949).

More recently, Samsonov and Popova (1957) have synthesized ThS and Th_2S_3, claiming that these are the most stable sulphides in the system, and that the sesquisulphide has a homogeneity range of $ThS_{1\cdot22-1\cdot59}$.

(*b*) *Th-Se System*

This was investigated by D'Eye, Sellmann, and Murray (1952). The compounds were synthesized from the elements, and after the initial reaction had taken place, 1 hr at 900 °C was allowed for equilibration. The thorium metal contained approximately 5 per cent. ThO_2, and ThOSe was observed as dark crystals in all the preparations. $ThSe_{2\cdot0}$ and $ThSe_{1\cdot7}$ were formed by degradation of the highest selenide, $ThSe_{2\cdot33}$, and the lower selenides by direct reaction of appropriate amounts of thorium and selenium. X-Ray crystallographic data were given by D'Eye (1953) for the four lower selenides.

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(c) *Th-Te System*

The only systematic work reported to date has been that of D'Eye and Sellmann (1954). Synthesis from the elements was carried out as in the Th-Se system. As in the previous system, samples were contaminated with ThOTe. All Th-Te compounds were observed to degrade below 1000 °C to the elements. The only structure given was that of $ThTe_{1\cdot0}$.

The monotelluride has also been synthesized by Ferro (1955), whose structure agrees well with that of D'Eye and Sellman. Both papers note the reactivity of the ThTe in air.

TABLE 1

THE SYSTEMS Th-S, Th-Se, AND Th-Te AS REPORTED IN THE LITERATURE

Type	Sulphides		Selenides	Tellurides
	Strotzer and Zumbusch (1941)	Eastman *et al.* (1950), Zachariasen (1949)	D'Eye, Sellmann, and Murray (1952)	D'Eye and Sellmann (1954)
Poly- ..	$ThS_{2\cdot36}$	Nil	$ThSe_{2\cdot33}$	$ThTe_{2\cdot66}$
Di- ..	ThS_2 ($ThS_{2\cdot0-1\cdot75}$)	ThS_2 (fixed composition) Orthorhombic $PbCl_2$ type $a=4\cdot268$, $b=7\cdot264$, $c=8\cdot617$ A	$ThSe_2$ Orthorhombic $PbCl_2$ type $a=4\cdot99$, $b=7\cdot52$, $c=9\cdot40$ A	$ThTe_2$
Th_7X_{12}	Nil	Th_7S_{12} Hexagonal $P6_3/m$ $a=11\cdot063$, $c=3\cdot991$ A	Th_7Se_{12} Hexagonal $P6_3/m$ $a=11\cdot58$, $c=4\cdot36$ A	Nil
Sesqui-	Th_2S_3 ($ThS_{1\cdot5-1\cdot2}$)	Th_2S_3 (small range) Orthorhombic Sb_2S_3 type $a=10\cdot99$, $b=10\cdot85$, $c=3\cdot96$ A	Th_2Se_3 (small range) Orthorhombic Sb_2S_3 type $a=11\cdot34$, $b=11\cdot57$, $c=4\cdot27$ A	Nil
Mono- ..	$ThS_{0\cdot75-0\cdot5}$ NaCl type	$ThS_{1\cdot0}$ NaCl type, $a=5\cdot68$ A	$ThSe_{1\cdot0}$ NaCl type, $a=5\cdot875$ A	$ThTe_{1\cdot0}$ CsCl type, $a=3\cdot827$ A

Unsatisfactory features in the early work include: (i) the disagreement between workers in the system Th-S; (ii) the use of impure materials in the investigations; (iii) compositions denoted by formulae to an accuracy out of all proportion to that of the analytical methods employed (e.g. $ThS_{1\cdot622}$ referred to by Eastman *et al.* 1950); (iv) short heating times used for equilibration.

It was therefore considered desirable to reassess these three systems using pure thorium metal so that the chemical and crystallographic effects of relatively

large amounts of oxygen could be avoided. Some chemical and electrical properties of the compounds prepared have been described by Bear and McTaggart (1958) and McTaggart (1958).

II. Materials

High purity thorium metal powder containing about 8 per cent. ThO_2 was used as the starting material for the growth of a thorium filament by the Van Arkel–de Boer process. Following an investigation into the growth of high-purity thorium by a modification of this process (Scaife and Wylie 1958), a number of precautions such as special purification and drying of the iodine used, was taken.

The metal thus obtained was highly ductile and crystalline, and contained 0·346 per cent. tungsten (due to the initial tungsten filament) and only spectrographically detectable amounts of other elements.

Portion of this filament was converted into thorium hydride by heating in pure hydrogen at about 600 °C and then 350 °C. When the highest hydride formed, the material crumbled to a fine powder, from which the tungsten filament could be removed (tungsten forms no hydride under these conditions). Pumping to 10^{-5} mm at 700 °C reduced this thorium hydride to the metal, which was in the form of a fine powder.

Sulphur, selenium, and tellurium were prepared as previously reported by McTaggart and Wadsley (1958), where reference is also made to the methods of analysis and density determinations.

X-Ray powder diffraction data were obtained using a Guinier-type focusing camera. Since X-ray results throughout this investigation depend on powder data alone, only the size and shape of the unit cell can in general be presented.

III. Results and Discussion

(a) *$ThX_{max.}$ Compounds*

For the preparation of all the $ThX_{max.}$ compositions, lengths of the original thorium filament (containing 0·346 per cent. W) were reacted directly with excess sulphur, selenium, or tellurium, the temperatures used being: Sulphide, sulphur-rich end 400–420 °C, thorium-rich end 550 °C; selenide, uniformly at 600 °C; telluride, uniformly at 600 °C.

Times of the order of 2–3 weeks were employed to ensure complete reaction and reasonable growth of crystals. At the completion of the reaction period, the excess sulphur, selenium, or tellurium was sublimed off by heating the chalcogenide to 250–300 °C in the case of the sulphide, 350 °C for the selenide, and 450 °C for the telluride.

In the case of the sulphide, analysis indicated a compound of composition $ThS_{2\cdot5}$ (cf. $ThS_{2\cdot36}$ observed by Strotzer and Zumbusch 1941). Contrary to the observation of D'Eye, Sellmann, and Murray (1952) that excess selenium was driven off from the selenide only after some months of heating to 300 °C to leave a compound of formula $ThSe_{2\cdot33}$, we found that selenium separated rapidly at 350 °C to leave a compound of formula $ThSe_{2\cdot5}$ from which no further selenium separated after 1 week at 350 °C.

The unit cells of these materials were found to be tetragonal; the lattice constants were: $ThS_{2\cdot5}$, $a=5\cdot43$, $c=10\cdot15$ A; $ThSe_{2\cdot5}$, $a=5\cdot629$, $c=10\cdot764$ A. From systematic absences in the powder patterns, the space group was probably $P4_2/n$ or $P4_2/nmc$, but in the absence of single crystal data, no further structural information could be inferred. Assuming unit cell formulae Th_4S_{10} and Th_4Se_{10}, the calculated densities are $6\cdot90$ and $8\cdot34$ g/c.c. respectively. These agree well with the observed densities, $6\cdot92$ and $8\cdot21$ g/c.c.

With the telluride, two syntheses were carried out; one resulted in a material of gross formula $ThTe_{3\cdot5}$, from which tellurium readily sublimed to yield a material of formula $ThTe_{3\cdot05}$, and the other yielded material of formula $ThTe_{2\cdot95}$. Both gave sharp X-ray patterns, but since there was evidence for reaction of the material with air, giving ThO_2+Te, the second sample was exposed to X-rays under a film of paraffin oil. With one end of the reaction tubes heated to 600 °C, tellurium slowly sublimed from both samples until a composition corresponding to $ThTe_{2\cdot0}$ was reached. It seems probable that the highest telluride is $ThTe_3$, and that the $ThTe_{3\cdot5}$ sample contains excess tellurium. This is made more likely by the structural similarity of the material of this composition to the trichalcogenides of titanium, zirconium, and hafnium (cf. McTaggart and Wadsley 1958). The structure seems to be monoclinic, with $a=6\cdot14$ A, $b=4\cdot31$ A, $c=10\cdot44$ A, and $\beta=98\cdot4°$, but the indexing is not sufficiently accurate to remove ambiguity. Like the trichalcogenides mentioned above, $ThTe_3$ has a pronounced layer structure, with an *001* spacing in this case of $10\cdot36$ A. The density calculated from the monoclinic cell is $7\cdot44$ g/c.c., which is close to the observed density of $7\cdot40$ g/c.c.

The identification of the tritelluride resolves the anomaly in the electrical resistivity of this material reported earlier by McTaggart (1958) and also the slow rate at which tellurium sublimes off at 600 °C (Bear and McTaggart 1958). One of the reflections from $ThTe_3$ falls close to the position of the strongest tellurium reflection, and this resulted in an initial misinterpretation of the pattern. In the earlier papers all references to $ThTe_{2\cdot5}$ should read $ThTe_3$.

Analytical data for the $ThX_{max.}$ compounds are recorded in Table 2 (values of n in ThX_n are to nearest $0\cdot05$).

(*b*) *Dichalcogenides*

The di-compounds were formed by degradation of the $ThX_{max.}$ compound at 900 °C *in vacuo* for several hours ($ThTe_3$ as noted above degraded to $ThTe_{2\cdot0}$ slowly at 600 °C). All three dichalcogenides gave satisfactorily sharp X-ray patterns (cf. D'Eye's (1953) results with $ThTe_{2\cdot0}$).

The disulphide and diselenide crystallize in the orthorhombic $PbCl_2$-type structure as reported in work by Zachariasen (1949) and D'Eye (1953). The lattice spacings observed are: ThS_2, $a=4\cdot283$, $b=7\cdot275$, $c=8\cdot617$ A; $ThSe_2$, $a=4\cdot435$, $b=7\cdot629$, $c=9\cdot085$ A; in good agreement with Zachariasen (1949) and D'Eye (1953). Our unit cell is slightly larger in each case.

The ditelluride gave a complex pattern which could be indexed on a hexagonal cell having $a=8\cdot49$ A and $c=9\cdot01$ A. However, the experimental inaccuracy was such that this may be only a pseudo-cell.

It should be mentioned here, that when a sample of $ThTe_{2\cdot0}$ was heated to 800 °C *in vacuo* for a few weeks in an attempt to grow larger crystals, a new phase formed. The bulk of the sample was found by analysis to have a composition close to $ThTe_{1\cdot9}$; a small quantity of ThOTe was also present due apparently to diffusion of oxygen through the walls of the silica tube. Many lines in the X-ray pattern of the bulk material could be interpreted as (*hk0*) reflections corresponding to a hexagonal cell of edge $a=12\cdot33$ A, about the order of magnitude required for a hexagonal telluride of the Th_7X_{12} type; but a *c*-axis of the required magnitude could not be found. Most lines are accounted for if $c=13\cdot8$ A, but this cell is not altogether satisfactory.

Other details of the dichalcogenides are given in Table 2.

TABLE 2

ANALYSIS OF THE $ThX_{max.}$ AND ThX_2 COMPOUNDS

Compound	Appearance	Percentage Composition				
		Theoretical		Analysis		
		Th	X	Th	X	*n* (in ThX_n)
$ThS_{2\cdot5}$ ..	Brick-red with slight purple tint	74·25	25·75	74·2	25·75	2·50
$ThSe_{2\cdot5}$ ..	Very dark purple	53·93	46·07	52·9	46·9	2·60
$ThTe_3$ ..	Black powder	37·64	62·36	37·4	62·5	3·05
ThS_2 ..	Purple-brown	78·28	21·72	78·5	21·8	2·00
$ThSe_2$ ..	Dark purplish grey	59·41	40·59	59·0	40·5	2·00
$ThTe_2$ ..	Black	47·52	52·48	47·4	52·4	2·00

(*c*) *Th_7X_{12} Type*

The sulphides and selenides of gross formula Th_7X_{12} were synthesized from the elements, using the thorium powder described previously. After 2 weeks' heating to 800 °C, the silica tubes were opened in dry argon, and the contents of each thoroughly ground up. They were then re-evacuated and sealed and again heated to 800 °C for a further 7 days, during which period they were well shaken up three times. The X-ray patterns showed that in both cases the dichalogenide was formed, together with a phase of previously unreported structure. The Th_7X_{12} structure was not observed. Since it was not found in earlier work, no synthesis of Th_7Te_{12} was attempted. Insufficient pure thorium was available when it became desirable to do so, but it seems probable that this compound may exist under some conditions (see below).

In Section III (*b*) it was noted that $ThTe_{1\cdot9}$ heated in the presence of a small amount of oxygen formed a new compound having affinities with the structure reported for Th_7X_{12}. This may suggest that the non-appearance of this phase here is due to the absence of oxygen. It seems possible that this structure, along with those of the lower chalcogenides (see below), is stabilized by the inclusion of a small proportion of oxygen. The observations of Kramers (1952)

on the sesquisulphides of cerium support this contention ; Kramers found that Ce_2S_3 crystallized in two different structures depending on the presence or absence of a small oxygen impurity.

(*d*) *Th_2X_3 Type*

Samples of composition Th_2S_3, Th_2Se_3, and Th_2Te_3 were synthesized from the elements as above.

The only sesqui-compound formed was Th_2Te_3, which crystallized with a hexagonal cell having $a=12\cdot49$ A and $c=4\cdot354$ A. This cell is similar in shape to those reported for the Th_7X_{12} compounds (cf. Table 1), and the observed reflections are consistent with the same space group, $P6_3/m$. Assuming that the structures are, in fact, basically the same, the composition suggests a defect cation lattice. This is reasonable, since the possible thorium positions are fully occupied in the Th_7X_{12} structure. The calculated density for $Th_7Te_{10\cdot5}$ would be $8\cdot35$ g/c.c., compared with the observed density of $8\cdot6$ g/c.c. The discrepancy is probably due to the presence of some ThO_2, for the sample had stood for some months in a stoppered bottle before the density was determined. The stoichiometric composition Th_7Te_{12} would give too high a density, especially as it would have to be in association with ThTe, Th, or ThO_2 (calculated density for $Th_7Te_{12}=8\cdot89$ g/c.c.).

Th_2Te_3 degraded on heating *in vacuo* at 1050 °C for more than a day, but this degradation could be due to oxygen diffusing in at this temperature resulting in the type of reaction discussed by Bear and McTaggart (1958).

The sulphide and selenide patterns indicated the presence of ThX_2 and the unreported phase noted above ; the orthorhombic Sb_2S_3-type compounds found by previous workers were not observed.

(*e*) *$ThX_{1\cdot0}$ Type*

Samples corresponding to the formulae $ThS_{1\cdot0}$, $ThSe_{1\cdot0}$, and $ThTe_{1\cdot0}$ were synthesized from the elements as described under Th_7X_{12} type, but in no case did the previously reported cubic monochalcogenide make up more than a small proportion of the sample. Additional lines corresponded, in the case of the sulphides and selenides, to ThX_2 and the other phase found in the samples of composition up to Th_7X_{12} ; and in the case of the telluride, to Th_2Te_3 and a small amount of a face-centred cubic material, $a=5\cdot116$ A.

The synthesis of the telluride was repeated using material slightly contaminated with oxygen, and in this case the monotelluride structure accounted for about 40 per cent. of the sample, the remainder being Th_2Te_3 and a little ThOTe.

These results indicate (i) lack of equilibrium (from the number of phases present in the samples), and (ii) the non-stoichiometric nature of ThTe (from the distribution of phases in the second specimen). The latter observation accords with the results of Strotzer and Zumbusch (1941) for ThS. Th_2Te_3 is also probably non-stoichiometric as mentioned above.

Because of the thermal stability and high heats of formation previously observed for the sesqui- and monosulphides, it is difficult to explain why these

compounds are not formed under our conditions. One possible explanation, already advanced under ThX_2 compounds, requires the presence of small quantities of oxygen for the formation of these structures. Some further support is given to this hypothesis by the increased yield of ThTe in the sample contaminated with oxygen.

The complexity of the chalcogenide systems of the transition metals is only now being appreciated (Jellinek 1957), and the effects of different experimental variables on the ordering of vacancies, and on the formation of polymorphous forms, have yet to be evaluated.

From the present results, it would appear that equilibrium relationships would only be obtained for these systems by a comprehensive investigation in which full account was taken of (i) purity of materials; (ii) temperatures of formation and disproportionation of compounds (involving rapid quenching and/or high temperature X-ray work); and (iii) liquidus and solidus curves (involving thermal analysis).

IV. Acknowledgments

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SOME STUDIES IN INORGANIC COMPLEXES

VI. NICKEL(II) WITH 2-PICOLYLAMINE

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Summary

Complexes of the type Ni pic_2X_2, Ni $pic_2X_2.nH_2O$, and Ni $pic_3(ClO_4)_2.H_2O$ have been prepared and studied, where X is Cl, Br, or I and pic is the chelating ligand 2-picolylamine. Conductance measurements in nitrobenzene, nitromethane, methanol, and water show that the blue compounds Ni pic_2X_2, whilst being hexacovalent complexes in the solid state, are progressively ionized in the respective solvents as halogen is replaced by solvent molecules. Conductance measurements also verified a hexacovalent structure for the Ni pic_3^{2+} ion complex whose salts are bi-univalent electrolytes. Magnetic measurements show that all the complexes are paramagnetic with a mean moment of 3·0 B.M. Their absorption spectra in the near ultraviolet region are characteristic of that of the ligand. A study in the visible spectrum was also made.

I. INTRODUCTION

Since the base 2-picolylamine has the same functional groups as 2,2′-dipyridyl and 1,10-phenanthroline, it was thought feasible that stable five-membered ring systems with metal cations could be formed by chelation. A comprehensive review of phenanthroline and similar metal complexes has been given by Brandt, Dwyer, and Gyarfas (1954), whilst more recently nickel(II) complexes of 2-pyridinaldoxime were studied by Krause and Busch (1958). An investigation into metal complexes of pyridine-2-aldehyde alkylimines has also been carried out by Bähr and Döge (1957). When aqueous solutions of nickel halides are treated with 2-picolylamine a vivid blue colour is developed if the ratio of ligand to nickel atom does not exceed 2 to 1. From these solutions bright blue complexes of the formula Ni pic_2X_2 crystallize out, in which pic is the chelating ligand 2-picolylamine and X is the chloride or bromide. The corresponding iodo derivative is less soluble and forms a microcrystalline ochre-yellow powder. To obtain the corresponding chloro complex of dipyridyl, Pfeiffer and Tappermann (1933) heated the tris derivative *in vacuo* at 140 °C, as both bisdipyridyl and phenanthroline nickel(II) complexes undergo disproportionation in water. This phenomenon is not so marked in the case of 2-picolylamine complexes unless an anion like perchlorate is present, when purplish pink tris-2-picolylamine nickel(II) perchlorate monohydrate is precipitated. Dwyer and Gyarfas (1949) observed similar results with phenanthroline–nickel complexes. If 3 molecules of ligand to 1 of nickel atom are present in aqueous solution, a reddish

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colour develops and tris-2-picolylamine nickel complexes may be recovered as purplish pink salts. However, if aqueous solutions of the latter are heated to above 90 °C, a blue colour is developed which remains on cooling and the original Ni pic_3X_2 salts crystallize out on standing. This colour is probably due to the formation of the ion Ni $pic_2(H_2O)_2^{2+}$ and although Basolo and Dwyer (1954) isolated the iodide Ni $dipy_2(H_2O)_2I_2$ of the dipyridyl complex and Pfeiffer and Tappermann (1933) and Pfeiffer *et al.* (1949) obtained the corresponding blue

TABLE 1

MOLECULAR CONDUCTIVITIES OF NICKEL(II) COMPLEXES AT 25 °C IN NITROBENZENE AND IN NITROMETHANE

Substance	Conductivity in Nitrobenzene (mhos)	M Conc. $\times 10^{-3}$	Conductivity in Nitro methane (mhos)	M Conc. $\times 10^{-3}$
Ni pic_2Cl_2	10·8	0·9	34·1	1·7
Ni pic_2Br_2	10·2	0·4	33·8	1·5
Ni pic_2I_2	11·4	0·8	35·8	1·3
Ni $pic_2Cl_2.2H_2O$ ..	46·3	2·1		
Ni $pic_2Br_2.2H_2O$ ..	46·0	1·9		
Ni pic_2I_2	48·9	0·8		
Ni $pic_2(ClO_4)_2.H_2O$ ..	45·2	1·4		

TABLE 2

MOLECULAR CONDUCTIVITIES OF NICKEL(II) COMPLEXES AT 25 °C IN METHANOL AND IN WATER

Substance	Conductivity in Methanol (mhos)	M Conc. $\times 10^{-2}$	Conductivity in Water (mhos)	M Conc. $\times 10^{-2}$
Ni pic_2Cl_2	97·7	2·9	219	9·1
Ni pic_2Br_2	96·0	5·1	223	7·6
Ni pic_2I_2	99·2	1·5	211	18·1
Ni $pic_2Cl_2.2H_2O$ ..	205	1·3	258	2·2
Ni $pic_2Br_2.2H_2O$ ..	194	2·4	253	2·5
Ni pic_2I_2	197	1·9	253	5·4
Ni $pic_2(ClO_4)_2.H_2O$ ..	203	1·1	228	2·3

phenanthroline complexes Ni $phen_2(H_2O)_2Cl_2.3H_2O$ and Ni $phen_2(H_2O)_2(ClO_4)_2$, no salts of the ion Ni $pic_2(H_2O)_2^{2+}$ were isolated. This may be due to the lesser solubility of the Ni pic_3^{2+} salts, although the possibility of *cis-trans*-isomerism must not be overlooked, since the ligand is unsymmetrical. The structure of the latter ion as a trischelate hexacovalent complex was verified by conductance methods in nitrobenzene, methanol, and water, and the results, which are given in Tables 1 and 2, show that its salts are bi-univalent electrolytes. Repetitive

analytical data showed that both the chloride and bromide as well as the perchlorate crystallize as hydrates, the water molecules being lost with rupture of the crystal lattices at temperatures a little above 100 °C, leaving purplish pink microcrystalline powders. Conductance measurements on the bischelate complexes Ni pic_2X_2 in the aforementioned solvents as well as in nitromethane indicated that, whilst the compounds are hexacovalent in the solid state with halogens occupying two coordinating positions, some ionization takes place at the necessarily low concentrations in nitrobenzene and nitromethane. The values obtained were about half of the limiting values for uni-univalent electrolytes, and this would indicate that some halide replacement by solvent molecules

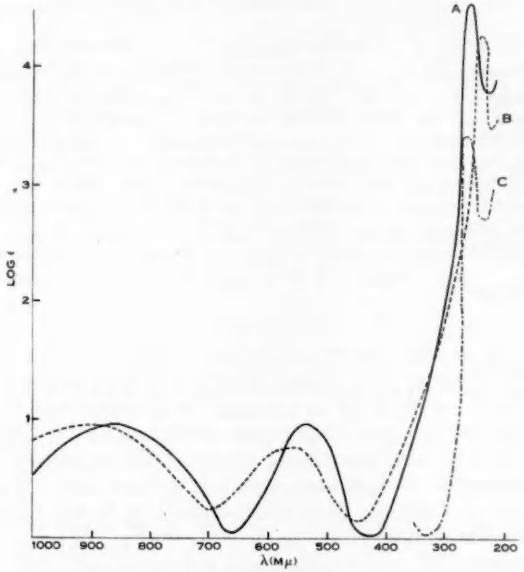

Fig. 1.—Molecular extinction coefficient against wavelength.

takes place. This is more marked when water and methanol are used as solvents, as even at relatively high concentrations the conductance measurements are close to the limiting values for a uni-univalent electrolyte in the latter case, and correspond to those for a di-univalent electrolyte in the former. In water there is little doubt that the ion Ni $pic_2(H_2O)_2^{2+}$ exists, although replacement by halide takes place as the Ni pic_2X_2 complexes crystallize out. The molecular conductivities of these complexes are summarized in Tables 1 and 2, and the conclusions drawn are on the assumption that the approximate molecular conductivities at infinite dilution for uni-univalent electrolytes in the aforementioned solvents are nitrobenzene 20, nitromethane 60, methanol 105, and water 135 $mhos^{-1}$ respectively. Molecular or ionic weights were indeterminable for reasons of low solubility in suitable solvents, but the possibility of the existence

of the dimers (Ni pic_3)(Ni $picX_4$) is discounted for reasons of low conductivity and the inability to precipitate the anion complex with triphenylmethylarsonium cation. Spectroscopic absorption studies were made with both the bis- and trischelate derivatives in aqueous solution in both the visible and near ultra-violet region. The curves obtained by plotting the logarithm of the molecular extinction coefficient (against the wavelength in millimicrons) are given in Figure 1, whilst the maxima and minima of the absorption curves are summarized

TABLE 3

ABSORPTION SPECTRA OF NICKEL(II) COMPLEXES IN WATER

Substance	Maxima	Minima
Ni pic_3^{2+}	260, 536, 860	225, 433, 675
Ni $pic_2(H_2O)_2^{2+}$ ..	259, 655, 905	225, 445, 695
2-Picolylamine ..	259	225, 325

in Table 3. Since the curves for the three halide complexes Ni pic_2X_2 in aqueous solution are identical, the evidence for the existence of the Ni $pic_2(H_2O)_2^{2+}$ ion is again very strong. It will be observed that the principal absorption peaks for the ligand and the Ni $pic_2(H_2O)_2^{2+}$ and Ni pic_3^{2+} ions lie within the range 240–260 mμ, the latter complex having a shift of absorption to slightly longer wavelength, which could indicate a greater stability. Measurements of magnetic susceptibility, which are summarized in Table 4, show that all the complexes

TABLE 4

MAGNETIC SUSCEPTIBILITIES CORRECTED TO 20 °C

Substance	$\chi_g \times 10^{-6}$	$\chi_M \times 10^{-6}$	$\chi_{M_1} \times 10^{-6}$	μ (B.M.)
Ni pic_2Cl_2	11·0	3800	3924	3·03
Ni pic_2Br_2	8·5	3695	3840	3·01
Ni pic_2I_2	6·9	3645	3810	2·98
Ni $pic_2Cl_2.2H_2O$ ..	7·4	3630	3827	3·00
Ni $pic_2Br_2.2H_2O$ ..	6·4	3700	3916	3·03
Ni pic_2I_2	5·7	3630	3857	3·02
Ni $pic_2(ClO_4)_2.H_2O$ ..	6·2	3720	3906	3·03

are paramagnetic with a mean moment of about 3·0 Bohr magnetons at 20 °C for the nickel atom. Although the calculated value on a spin-only basis is 2·83 B.M., as Nyholm (1953) has pointed out, this is not unexpected when the octahedral attachment is unsymmetrical. Since there is likely to be little double bond character in paramagnetic nickel complexes involving the use of *4d* orbitals in bond formation, there would be little release in the restraint on electrons and only a slight shift in absorption to longer wavelength would be expected. This agrees with the absorption curves obtained, which are

characteristic of the ligand rather than of the nickel atom in the near ultraviolet region. The lack of absorption at or about 400 mμ is also in agreement with Nyholm's (1954) observation that a sharp absorption band in this region is characteristic of diamagnetic nickel(II) complexes, although Katzin (1958, 1959) has associated absorption at this wavelength with octahedrally coordinated nickel(II) and has maintained that a shift of absorption to slightly lower wavelengths takes place when tetrahedral nickel complex formation results. However, the latter conclusions are based on studies of ethylenediamine complexes in which any absorption must be due to the nickel atom, since this ligand gives no absorption in this region, unlike 2-picolylamine. Dwyer and Mellor (1941) have pointed out that paramagnetic tetracovalent nickel(II) complexes tend to become hexacovalent, since no electron promotion is necessary when upper *d* orbitals are used for bond hybridization, and this would account for the non-existence of $Ni\,pic_2(ClO_4)_2$. Attempts to form 2-picolylamine–nickel complexes of higher oxidation state were unsuccessful, as is not unexpected with paramagnetic nickel. The complexes $Ni\,pic_2X_2$ were found to be slightly soluble in methanol, ethanol, and 1,4-dioxane, giving pale blue solutions. They are slightly soluble in pyridine and 2-picoline, forming orange coloured solutions, indicating some ligand replacement by solvent molecules. The salts of the ion $Ni\,pic_3^{2+}$ are soluble in pyridine and 2-picoline, being only sparingly soluble in methanol, acetone, and 1,4-dioxane. Both types of complexes are almost insoluble in other common organic solvents. The complexes $Ni\,pic_2X_2$ are stable to above 300 °C, whilst the salts of the $Ni\,pic_3^{2+}$ ion complex were found to decompose at temperatures ranging from 255 °C (perchlorate) to 300 °C (iodide).

Further studies with the ligand 2-picolylamine and other transition metals are proceeding.

II. Experimental

Conductance measurements and solvent purifications were carried out according to the methods outlined in previous papers. Measurements of absorption spectra were made with a Beckmann quartz spectrophotometer, model DU. Magnetic measurements were determined by the Gouy method.

(*a*) *Dichlorobis-(2-picolylamine)nickel(II)*.—A solution of nickel chloride (1·30 g ; 10 mmole) in water (10 ml) was treated with 2-picolylamine (2·16 g ; 20 mmole) with shaking. The brilliant blue solution which formed was evaporated to half-volume and set aside to crystallize. The bright blue acicular crystals which formed on standing were washed three times with ethanol and dried in an oven at 100 °C. Additional product was obtained by evaporation of the residual solution. The yield (2·92 g) was not quantitative since the remaining solution was rejected (Found : C, 41·7 ; H, 4·9 ; Cl, 20·2%. Calc. for $C_{12}H_{16}N_4Cl_2Ni$: C, 41·7 ; H, 4·7 ; Cl, 20·5%).

(*b*) *Dibromobis-(2-picolylamine)nickel(II)*.—The above procedure was repeated with the addition of lithium bromide (3 g), prior to treating with the ligand. The blue solution yielded bright blue acicular crystals (yield 3·94 g) (Found : C, 33·0 ; H, 3·6 ; Br, 36·6%. Calc. for $C_{12}H_{16}N_4Br_2Ni$: C, 33·2 ; H, 3·7 ; Br, 36·9%).

(*c*) *Di-iodobis-(2-picolylamine)nickel(II)*.—Procedure (*a*) was repeated with the addition of lithium iodide (3 g) prior to evaporation. The blue solution yielded buff coloured crystals (yield 5·11 g) (Found : C, 27·4, 27·3 ; H, 3·1, 3·0 ; I, 47·6%. Calc. for $C_{12}H_{16}N_4I_2Ni$: C, 27·3 ; H, 3·1 ; I, 48·0%).

(*d*) *Tris-(2-picolylamine)nickel(II) Chloride Dihydrate.*—Procedure (*a*) was repeated using 2-picolylamine (3·24 g ; 30 mmole). The blue colour changed to a deep red, and on partial evaporation to half-volume purple-pink macrocrystals belonging to the cubic system were formed. These were washed with ethanol and dried at 100 °C (yield 4·21 g) (Found : C, 44·2 ; H, 5·6 ; Cl, 14·7%. Calc. for $C_{18}H_{28}N_6Cl_2O_2Ni$: C, 44·1 ; H, 5·8 ; Cl, 14·4%). The anhydrous salt decomposed at 268 °C.

(*e*) *Tris-(2-picolylamine)nickel(II) Bromide Dihydrate.*—Procedure (*b*) was repeated using 2-picolylamine (3·24'g ; 30 mmole). Violet-pink octahedra macrocrystals were obtained (yield 4·81 g) (Found : C, 37·5 ; H, 5·0 ; Br, 27·3%. Calc. for $C_{18}H_{28}N_6Br_2O_2Ni$: C, 37·3 ; H, 4·9 ; Br, 27·6%). The anhydrous salt decomposed at 270 °C.

(*f*) *Tris-(2-picolylamine)nickel(II) Iodide.*—Procedure (*c*) was repeated using 2-picolylamine (3·24 g ; 30 mmole). Purplish pink octahedra were obtained from the red solution which formed (yield 6·03 g) (Found : C, 33·9 ; H, 3·6 ; I, 40·3%. Calc. for $C_{18}H_{24}N_6I_2Ni$: C, 33·9 ; H, 3·8 ; I, 39·9%). The salt decomposed at 300 °C.

(*g*) *Tris-(2-picolylamine)nickel(II) Perchlorate Monohydrate.*—A solution containing nickel nitrate (1·83 g ; 10 mmole) in water (10 ml) was treated with 2-picolylamine (3·24 g ; 30 mmole) and sodium perchlorate (3 g) in water (5 ml) added. On shaking and allowing to stand, rose-pink cubic crystals settled out from the violet-red solution which formed. These were washed with a little alcohol and dried at 100 °C (yield 5·17 g). Carbon and hydrogen analyses were determined on separate preparations (Found : C, 35·9, 35·9 ; H, 4·3, 4·3 ; Ni, 10·0%. Calc. for $C_{18}H_{26}N_6Cl_2O_9Ni$: C, 36·0 ; H, 4·4 ; Ni, 9·8%). The anhydrous salt decomposed at 255 °C.

III. Acknowledgment

The author wishes to thank Dr. E. Challen of the Microanalytical Laboratory for most of the carbon and hydrogen analyses.

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STUDIES IN WAXES

XIV. AN INVESTIGATION OF THE ALIPHATIC CONSTITUENTS OF HYDROLYSED WOOL WAX BY GAS CHROMATOGRAPHY

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Summary

A quantitative analysis has been made of the composition of each of the classes of aliphatic constituents known to exist in hydrolysed wool wax. These classes consist of α-hydroxy acids, ω-hydroxy acids, alkanoic acids, monohydric alcohols, and α,β-diols. Each has been found to contain members of the normal, *iso*-, and *anteiso*-homologous series of compounds.

The analysis was carried out by saponification of the wax and separation of the constituents into the above classes which were separately reduced to the corresponding hydrocarbon mixtures. The composition of these mixtures was determined by gas chromatographic separation.

I. Introduction

As the result of many investigations an almost complete knowledge has now been obtained of the types of compounds present in hydrolysed wool wax (Horn and Ilse 1956*a*, 1956*b*), and a remarkable number of compounds has been isolated and identified (Weitkamp 1945 ; Horn and Hougen 1951, 1953 ; Murray and Schoenfeld 1952, 1955 ; Horn *et al.* 1954 ; Horn and Pretorius 1956).

Low pressure fractional distillation has been the principal means of separating these compounds, and frequent reference has been made to the inability to separate minor or close-boiling constituents or to distil without decomposition those of higher molecular weight. It was considered likely then that a number of constituents remained to be identified as suggested by Hatt (1958), and that this could now be easily done by gas chromatography, which method would also give a quantitative analysis. Accordingly a sample of fresh wool wax has been saponified and the hydrolysis products separated into the alkanoic acids, α-hydroxy acids, ω-hydroxy acids, monohydric alcohols, and α,β-diols. Each of these mixtures was reduced to the corresponding mixture of hydrocarbons which was analysed by gas chromatography.

II. Experimental

Light petroleum refers to a fraction of boiling range 60–80 °C. Except where stated alumina (type H, Peter Spence and Sons Ltd., Widnes, England) was of Brockman activity II.

(*a*) *Origin of the Wax.*—The wax was obtained from the fleece of a Merino ewe which had not been dipped for 3 years and which had worn a canvas covering during the 12 months since the previous shearing. The inner third of the staple (1350 g) was cut off and extracted three times

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with hot, redistilled commercial hexane. The extracts were combined, filtered, and evaporated, finally at 100 °C and 0·2 mm pressure to give the inner fleece wax (232 g).

The wax (560 g) was also recovered from the outer two-thirds of the staple (2800 g), but was discarded when it was found that the steroids in this had suffered extensive autoxidation (cf. Horn and Ilse 1956*a*, 1956*b*).

(*b*) *Saponification and Separation of the Acid and Neutral Fractions.*—A portion of the wax (51·1 g) was saponified by the method of Barnes, Curtis, and Hatt (1952), and most of the unsaponifiable material was removed from the diluted mixture by four extractions with hot hexane. The hexane extracts were washed with 30% aqueous ethanol and then combined and evaporated. The combined aqueous solutions were treated with 10% aqueous calcium chloride solution (250 ml) and the calcium salts obtained in a granular form by evaporation of most of the liquid. The salts were collected, washed with water, dried, and crushed. They were extracted twice with acetone under reflux for 1 hr to give the remaining unsaponifiable material (2·15 g). The combined unsaponifiable material (26·5 g) had an hydroxyl value of 152.

(*c*) *Methylation of the Acid Fraction.*—The acids were converted directly to their methyl esters by refluxing the calcium salts with methanol, benzene, and a small amount of conc. sulphuric acid. This method had previously been developed in this laboratory to prepare the esters on a larger than laboratory scale (Downing, unpublished data). It avoids the formation of estolidic material from the hydroxy acids which always occurs when the free acids are isolated. It is similar to the recently published method of Miyakawa, Noguchi, and Namizu (1956), but the products obtained by these workers had higher acid numbers than obtained in the present work. In detail the whole of the finely-powdered calcium salts obtained in (*b*) above were refluxed for 3 hr with methanol (A.R., 300 ml), benzene (A.R., 300 ml), and conc. sulphuric acid (6 ml). The mixture was then filtered from calcium sulphate, washed five times with 25% aqueous ethanol, and the benzene distilled off, the last traces being removed at 100 °C and 100 mm pressure. The residual methyl esters (26·0 g) had an acid value of 1·0 and an hydroxyl value of 67·5.

(*d*) *Reduction of the Methyl Esters and Chromatography of the Resulting Alcohols.*—An attempted separation of the hydroxy and non-hydroxy acid methyl esters by chromatography on alumina was unsuccessful owing to hydrolysis of the esters, which even occurred on acid-washed alumina. It was also considered that this separation by means of counter-current solvent distribution was insufficiently complete for application to this work (Horn *et al.* 1954). The methyl esters were therefore reduced with lithium aluminium hydride and the resulting monohydric alcohols and diols separated by chromatography on alumina (Horn *et al.* 1954).

The hydride reduction was performed in high yield (98%). The resulting alcoholic mixture had an hydroxyl value of 240, and its infra-red spectrum showed no trace of carboxyl absorption. A portion of this mixture (11·4 g) was cleanly resolved by chromatography on alumina into three fractions: (i) monohydric alcohols (6·84 g; hydroxyl value 171) eluted by chloroform-benzene (1 : 2); (ii) α,ω-diols (0·60 g; m.p. 101–108 °C; hydroxyl value 246) eluted by chloroform-ethanol (2 : 1); and (iii) α,β-diols (3·1 g) eluted by further quantities of chloroform-ethanol. Although there appeared to have been no overlapping between fractions (ii) and (iii), to be quite sure of the separation of the two types of diols, fraction (iii) was treated with acetone and a trace of sulphuric acid to convert the α,β-diols to ketals. These were chromatographed on alumina and eluted with light petroleum. Hydrolysis gave the fraction of refined α,β-diols (2·73 g; m.p. 65–70 °C; hydroxyl value 400).

(*e*) *Fractionation of the Unsaponifiable Material.*—The bulk of the aliphatic material was separated from a portion of the unsaponifiable fraction by a urea treatment in the manner of von Rudloff (1951). The adducted material (1·39 g) was then chromatographed on alumina. Light petroleum eluted a small amount (0·03 g) of wax (m.p. 61–62 °C) whose infra-red spectrum indicated the presence only of saturated hydrocarbons. The monohydric alcohols (0·96 g; hydroxyl value 143) were eluted, as above, by chloroform-benzene (1 : 2) and the α,β-diols by chloroform-ethanol (2 : 1). The latter were further refined by chromatography of their ketals as described earlier. The resulting product of α,β-diols (0·15 g) had m.p. 70–74 °C and an hydroxyl value of 317·5.

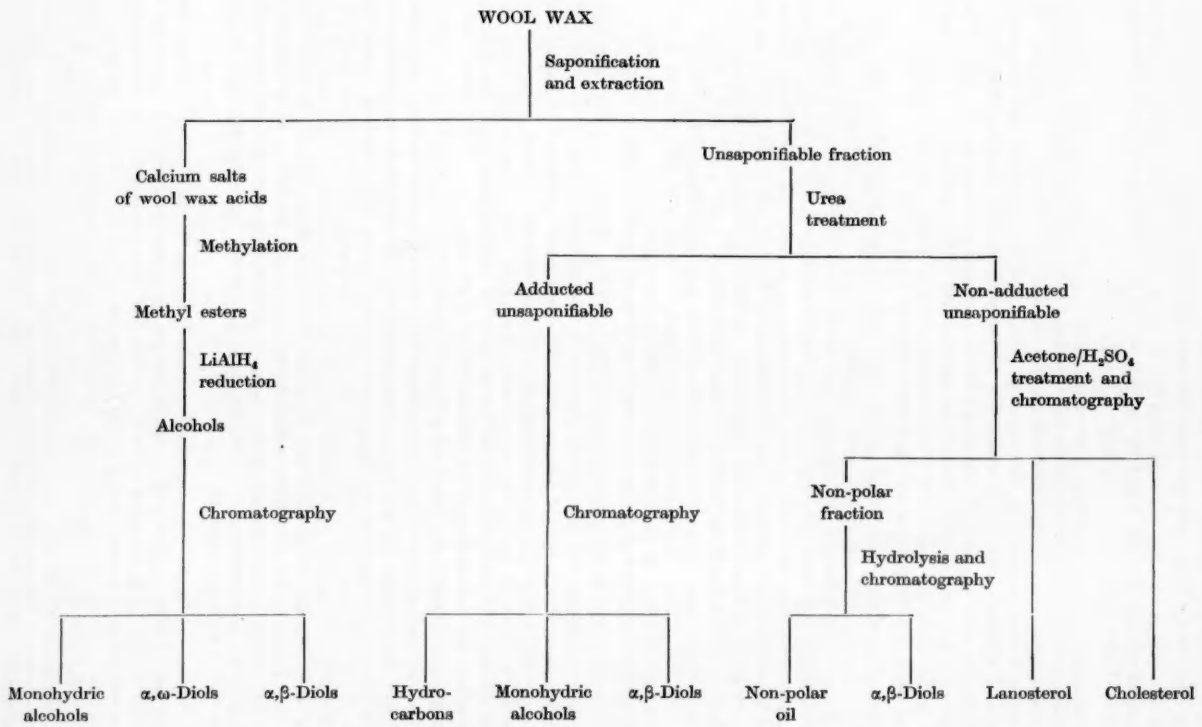

Fig. 1.—Fractionation of wool wax into classes of constituents.

The portion of the unsaponifiable fraction which failed to form an adduct with urea (8·8 g) was treated with acidified acetone to form the ketals of those α,β-diols not removed in the urea separation, and the product was chromatographed on alumina. Light petroleum eluted an oil (1·0 g), benzene eluted the lanosterol fraction (the mixture of lanostenol and lanostadienol, 4·4 g), chloroform eluted cholesterol (3·13 g), and a trace of gum (0·02 g) was finally eluted by a chloroform–ethanol mixture. The recovery was 97%. Elution of the sterols was followed by the modified Liebermann-Burchard reaction of Luddy, Turner, and Scanlan (1953). The oily light petroleum eluate was taken up in ethanol containing a trace of hydrochloric acid and the solvent was slowly distilled off on the steam-bath. The residue (0·93 g) was chromatographed on alumina. Light petroleum eluted an oil (0·36 g) and chloroform–ethanol (2 : 1) eluted the non-urea-adducted α,β-diols (0·51 g). The oily light petroleum eluate did not form a urea adduct. It proved non-volatile when examined by gas chromatography at 260 °C. It gave a strong yellow colour with the Liebermann-Burchard reaction. Its infra-red spectrum showed the presence of carbonyl and conjugated carbonyl groupings.

TABLE 1

COMPOSITION OF ACID AND UNSAPONIFIABLE FRACTIONS OF WOOL WAX

Composition	Weight (%)	Horn and Ilse (1956) Weight (%)
A: Acid fraction		
Alkanoic acids	60	60
ω-Hydroxy acids	5	32·5
α-Hydroxy acids	30	
Undetermined	5	7·5
B: Unsaponifiable fraction (51·8% by wt. of wax)		
(i) Urea-adducted	(13·7)	14·7
Hydrocarbons	0·3	0·9
Monoalcohols	9·5	—
α,β-Diols	1·5	—
(ii) Not urea-adducted		
Cholesterol	31	32·5
Lanosterol	44	44·2
α,β-Diols	5	3·2
Undetermined	8·7	4·5

The fractionation procedure described above is set out in Figure 1 and the quantitative results from it are summarized in Table 1.

(*f*) *Conversion to Hydrocarbons.*—Each of the mixtures of aliphatic alcohols produced by the fractionations above was reduced to the corresponding mixtures of hydrocarbons by conversion to the iodides which were reduced with lithium aluminium hydride. The iodides were prepared by heating the alcohols at 100 °C with iodine (2-fold excess) and red phosphorus (20% of wt. of iodine). After 1 hr the remaining iodine was evaporated at 100 °C under reduced pressure. The residue was taken up in light petroleum, the solution washed with water, dried over sodium sulphate, and the solvent evaporated. The recovered material was dissolved in ether (A.R.) and an excess of lithium aluminium hydride was added. After standing overnight, the unreacted hydride was destroyed with ethyl acetate, the solution washed with dilute sulphuric acid, and the solvent evaporated. The residue was refluxed for 30 min with 0·5N ethanolic potassium hydroxide solution to hydrolyse possible traces of unchanged iodides. The recovered material was then

chromatographed on alumina. Light petroleum eluted the hydrocarbons in overall yields of 80–90%.

The hydrocarbon mixture from the monoalcohols of the reduced acid fraction was found to be contaminated with a slightly more polar material which, from its infra-red absorption at 1125 cm^{-1} and gas chromatographic behaviour, appeared to be the ethyl ethers of the long-chain alcohols formed by reaction of unchanged iodides with ethoxide. This material was readily removed by chromatography on alumina of higher activity (Brockmann I).

The hydrocarbon mixture obtained by reduction of the α,β-diols showed considerable absorption in its infra-red spectrum due to unsaturation. Most of this was α-olefinic (905 cm^{-1}) with some *trans*-forms of isomeric olefines (965 and 1635 cm^{-1}). The mixture was therefore completely hydrogenated with Adams's catalyst in ethyl acetate at room temperature and atmospheric pressure.

The hydrocarbon mixtures derived from the remaining alcoholic fractions showed only saturated hydrocarbon absorption in their infra-red spectra.

As a general check on the reduction to hydrocarbons by way of the iodides the monohydric alcohols from the reduced acid fraction were reduced by an alternate route. This consisted of the preparation of the tosylates and their reduction by lithium aluminium hydride in the usual way. The composition of the hydrocarbon mixtures obtained by the two methods were found to be in close agreement as shown in Table 4.

TABLE 2

REFERENCE HYDROCARBONS

Series and Carbon No.	Wt. of Alcohol Taken (mg)	Wt. % Calc. as Hydro-carbon	Wt. % Found	Series and Carbon No.	Wt. of Alcohol Taken (mg)	Wt. % Calc. as Hydro-carbon	Wt. % Found
iso-20	23·6	10·0	10·7	*anteiso*-17	25·0	10·4	10·1
22	25·5	10·8	11·3	20	25·7	10·9	11·6
24	29·0	12·3	12·7	23	28·8	12·1	12·8
26	23·8	10·2	8·9	25	25·3	10·8	10·3
				27	29·0	12·4	11·6

(*g*) *Reference Hydrocarbons.*—A synthetic mixture of *iso*- and *anteiso*-hydrocarbons was prepared by mixing the pure alcohols, isolated from wool wax during an earlier investigation (Murray and Schoenfeld 1952), and reducing the mixture as described above (see Table 2). A series of synthetic normal hydrocarbons was provided by Dr. R. J. Meakins, Division of Electrotechnology, C.S.I.R.O.

(*h*) *Gas Chromatographic Technique.*—(i) *Apparatus.* The columns were heated in a temperature-controlled, well-stirred air-bath. The detector, heated independently of the columns and maintained at 260 °C, was a new design of the Martin and James gas density meter (Murray 1959). The sample was introduced by $\frac{1}{8}$ in. dia. stainless steel rod probes provided with calibrated capillary tips and were inserted through a valve into the preheater held 10–20 °C above the column temperature.

The column was of copper tubing, 8 ft in length and 0·17 in. bore, and was coiled after packing. The stationary phase (10% by wt. of the packing) was Silicone Elastomer E 301 (Griffin and George Ltd., London) and was supported on Celite 545 graded to 60–85 mesh (B.S.S.) and water-washed. A similar column was used in the reference circuit.

(ii) *Programmed Heating of Columns.* Since the constituents of the hydrocarbon mixtures covered a wide range of carbon number, programmed heating of the columns was used as well as operation at constant temperature. The chromatograms obtained by programmed heating gave a clearer overall representation of the compositions, the separation was slightly better, and since

the peaks were more of one shape, the quantitative estimation based on them was undoubtedly more accurate.

The means for raising the temperature of the columns in an almost linear fashion has been described (Desty 1958). The range covered by the chromatograms was 100–265 °C, but to take up the backlash in the mechanism the heating was actually begun at about 95 °C, and the sample injected at 100 °C.

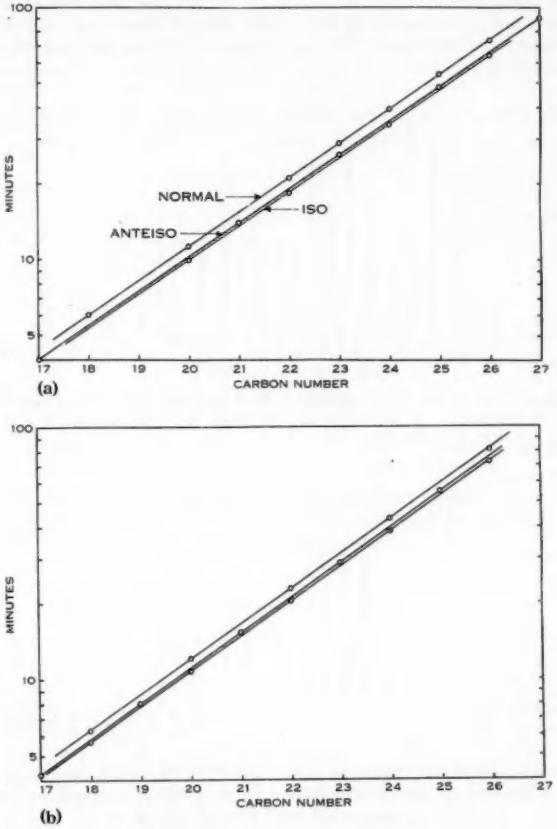

Fig. 2.—(*a*) Retention times of normal, *iso*- and *anteiso*-reference hydrocarbons (at 220 °C and 500 mm N_2 pressure) plotted on log scale against carbon number. (*b*) Retention times of the hydrocarbons derived from the non-hydroxylated acids (at 220 °C and 500 mm N_2 pressure) plotted on log scale against carbon number.

(iii) *Subtraction of Normal Hydrocarbons.* Advantage has been taken in this work of the ability of Linde Molecular Sieve Type 5A to absorb normal hydrocarbons from the gaseous sample stream, and allow the passage of the branched hydrocarbons (Whitham 1958). A short copper column 8 in. in length and 0·17 in. bore was packed with Linde Molecular Sieve Type 5A (Fisher

Scientific Co., U.S.A.) crushed and sieved to 40–60 mesh (B.S.S.). It was inserted into the column air-bath and coupled to the outlet of the chromatographic column. When first tested at 270 °C it passed squalane but totally absorbed the singly-branched *iso-* and *anteiso*-reference hydrocarbons. This affinity for the singly-branched hydrocarbons was destroyed by repeated passage of 5 μl samples of the reference hydrocarbons until no absorption occurred. The column then retained only the normal compounds and remained unchanged for the duration of the work.

(iv) *Identification of Hydrocarbons.* Only the normal, *iso-*, and *anteiso*-series of aliphatic compounds have been previously reported in wool wax, all three series being represented in the non-hydroxylated acids (Weitkamp 1945) and the monohydric alcohols (Murray and Schoenfeld

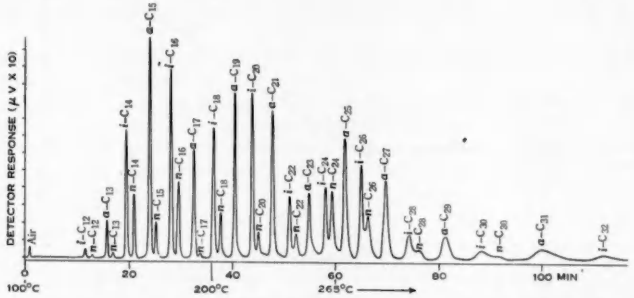

Fig. 3.—Chromatogram of the hydrocarbons derived from the non-hydroxylated acids. Column temperature 100→265 °C; N_2 pressure 500 mm; charge 2·5 μl.

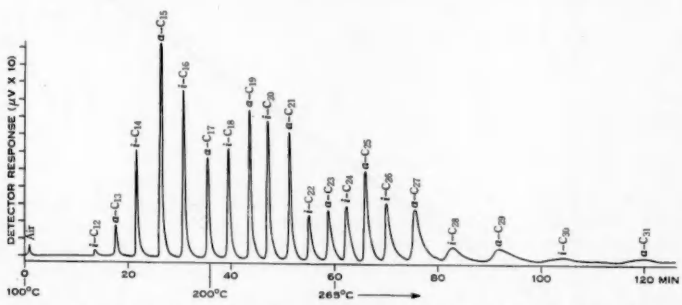

Fig. 4.—Chromatogram of the hydrocarbons derived from the non-hydroxylated acids. Normal hydrocarbons subtracted by a molecular sieve column. Column temperature 100→265 °C; N_2 pressure 520 mm; charge 2·5 μl.

1952, 1955). On preliminary examination of the hydrocarbon mixtures by gas chromatography it was apparent that likewise only these three series of hydrocarbons were present, and were represented in all the mixtures. Identification of the individual hydrocarbons was made as follows.

The mixtures were first examined at two constant column temperatures, 220 and 260 °C, and the retention times of the separated hydrocarbons (measured from the air peak) compared with those of the branched (C_{17}-C_{27}) and normal (C_{14}-C_{34}) reference hydrocarbon mixtures run separately. The detector was used at its maximum sensitivity to allow of the use of the smallest possible charge (usually 1–25 μl) and so avoid unsymmetrical peaks caused by overloading the column. It was found that the retention times for any particular hydrocarbon varied slightly,

owing probably to the daily rise in laboratory temperature. It was possible by comparison with the reference to determine easily its carbon number and whether it was normal, or singly-branched. However, it was not possible to determine whether it was *iso* or *anteiso*, as members of these series have too small a difference in retention time.

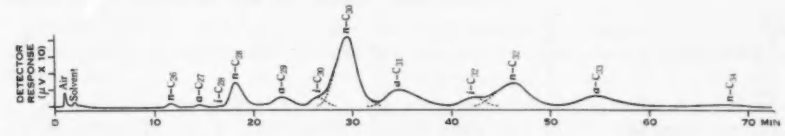

Fig. 5.—Chromatogram of the hydrocarbons derived from the ω-hydroxy acids. Column temperature 270 °C; N_2 pressure 600 mm; charge 1 μl.

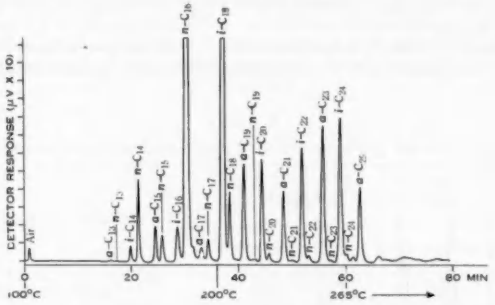

Fig. 6.—Chromatogram of the hydrocarbons derived from the α-hydroxy acids. Column temperature 100→265 °C; N_2 pressure 500 mm; charge 2·5 μl.

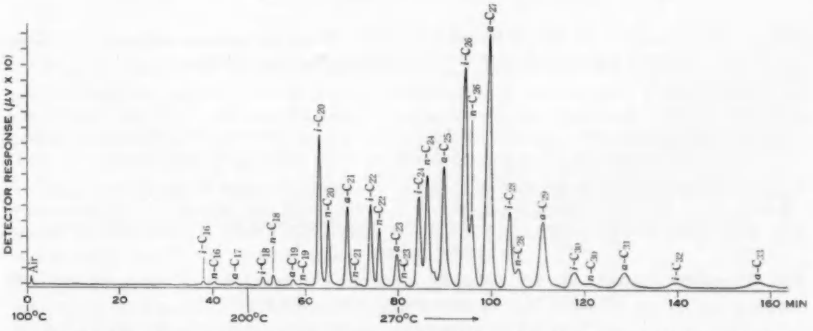

Fig. 7.—Chromatogram of the hydrocarbons derived from the monohydric alcohols. Column temperature 100→270 °C; N_2 pressure 500 mm; charge 2·5 μl.

This daily variation would be at a minimum in a single run (of approximately 60 min) and so the retention times for the hydrocarbons in each run were plotted on a log scale against their carbon numbers already determined. As first noted by Martin and James (1952), and later by others, members of an homologous series so plotted lie on a straight line. Figure 2 (*a*) shows the reference hydrocarbons plotted in this manner and Figure 2 (*b*) the hydrocarbons derived from the

wool-wax alkanoic acids. The *anteiso*-compound has a shorter retention time than the normal compound and the *iso*-compound slightly shorter still. The same relation between normal, *iso*-, and *anteiso*-hydrocarbons of shorter-chain length (C_7 and C_8) chromatographed on *n*-hexatriacontane is observed in the results of Desty and Whyman (1957).

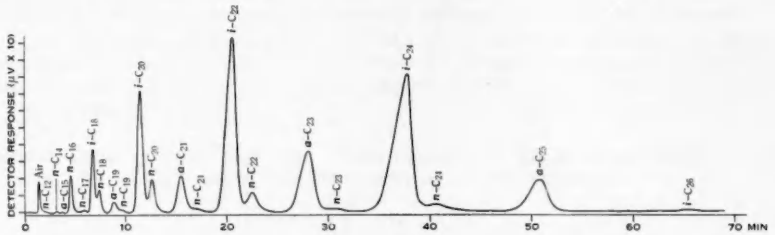

Fig. 8.—Chromatogram of the hydrocarbons derived from the urea-adducted α,β-diols. Column temperature 220 °C; N_2 pressure 500 mm; charge 2·5 μl.

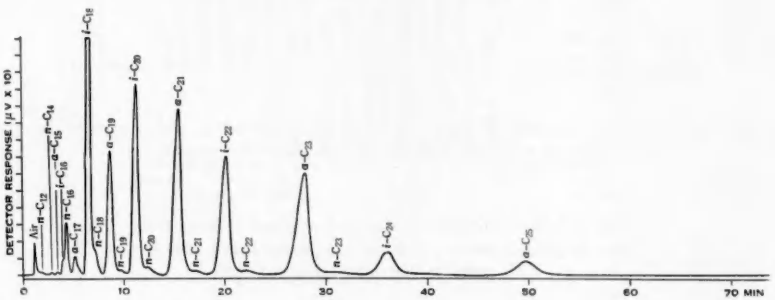

Fig. 9.—Chromatogram of the hydrocarbons derived from the non-urea-adducted α,β-diols. Column temperature 220 °C; N_2 pressure 500 mm; charge 2·5 μl.

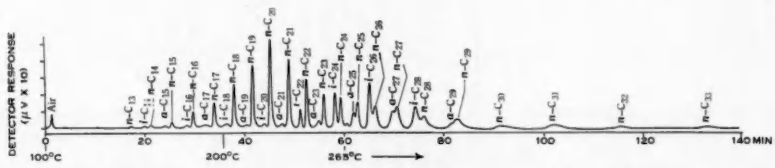

Fig. 10.—Chromatogram of the naturally occurring hydrocarbons. Column temperature 100→265 °C; N_2 pressure 500 mm; charge 2·5 μl.

All the hydrocarbon mixtures gave diagrams similar to Figure 2, and except in a few instances no difficulty was experienced in clearly differentiating between the *anteiso*-series, which were always of odd carbon number, and the *iso*-series whose members were always of even carbon number. A few of the minor branched components did not fall precisely on the straight lines of the branched series, but in all these cases the peaks were either small and ill-formed or were small shoulders on large peaks. These components were therefore classed as *anteiso* if they were found to be of odd carbon number and *iso* if they were of even carbon number in agreement with the above finding.

The mixtures were further examined using programmed heating of the column. Since these runs were of considerable length, the reproducibility of conditions was probably not as good as those at constant temperature. Consequently the samples were first run alone and then again combined with each of the reference mixtures. These runs provided much confirmatory evidence for the conclusions made from the constant temperature runs.

Finally, the use of the Linde molecular sieve column gave further confirmation of the results in distinguishing between normal and branched components as shown in a striking manner in Figures 3 and 4.

(v) *Quantitative Estimation.* Determination of the quantitative composition of the mixtures was made from the chromatograms shown in Figure 3 and Figures 5–10. The percentage which the area of each peak represents of the total area of all the peaks is its weight per cent. concentration in the mixture, after making a small correction for the molecular weight of nitrogen (James and Wheatley 1956). The areas were estimated by weighing the profiles of the peaks cut out of good quality paper. The proportions of the constituents were expressed as percentages of the total material eluted. For the mixture of *iso*- and *anteiso*-reference hydrocarbons, the overall process of reduction from the alcohols and chromatographic analysis produced results within $\pm 1 \cdot 3\%$ of the proportions weighed into the synthetic mixture (Table 2).

TABLE 3

CALCULATED AVERAGE MOLECULAR WEIGHTS OF MIXTURES OF ALCOHOLS

Source of Alcohols	Molecular Weight from	
	Chromatograms	Hydroxyl Values
Non-hydroxy acids ..	319	328
ω-Hydroxy acids.. ..	461	470
α-Hydroxy acids.. ..	288	281
Monoalcohols	371	392
α,β-Diols	328	354

The completeness of elution of the hydrocarbon mixtures was checked in the following manner. From the proportions found for the constituents of each mixture of hydrocarbons the mol. wt. of a mixture of alcohols of the same composition was calculated, and compared with that derived from the hydroxyl value of the original alcohol mixture. The general agreement of these two values showed that elution of the mixtures was practically complete (Table 3).

With the mixture of naturally occurring hydrocarbons, however, the completeness of elution was estimated by comparing the total peak area with that of a mixture known to be completely eluted, identical charges having been used. It was thus found that approximately only 30% of the charge was eluted up to a carbon number of 33.

The results of this investigation are summarized in Table 4 where they are compared with those of previous workers. The chromatograms shown in Figures 3–9 have also been included to give a clear visual representation of the composition of the fractions.

III. DISCUSSION

In the present investigation it has been found possible to provide a detailed estimate of the proportions of the aliphatic constituents in each of the fractions of wool wax. The difficulties encountered in other separation techniques have previously prevented similar estimates for most fractions, although Weitkamp

TABLE 4

HYDROCARBONS DERIVED FROM WOOL-WAX FRACTIONS (WT. %)

Hydrocarbon Series Carbon Number	Non-Hydroxylated Acids		ω-Hydroxy Acids	α-Hydroxy Acids	Naturally Occurring Hydrocarbons	Monohydric Alcohols	α,β-Diols
	Via Iodides	Via Tosylates					
n-12	0·1 (0·4)*	—	—	‡	—	—	—
13	0·2	Trace	—	Trace	Trace	—	—
14	1·9 (2·8)	1·2	—	2·3‡	0·3	—	0·1
15	1·2	0·9	—	0·9	0·4	—	—
16	2·5 (2·8)	1·9	—	39·7‡	1·8	0·1	2·2‖
17	0·2	Trace	—	0·7	2·7	—	Trace
18	1·5 (0·2)	1·0	—	2·1‡	4·8	0·5§	0·9
19	—	—	—	0·1	7·0	Trace	0·2
20	0·9 (0·6)	0·8	—	0·3	10·2	2·9§	1·0
21	—	—	—	0·1	7·7	0·1	0·4
22	0·8 (0·4)	1·0	—	0·3	5·5	2·6§	0·8
23	—	—	—	Trace	4·0	0·1	0·4
24	3·0 (1·2)	3·1	—	0·2	3·6	6·6§	0·4
25	—	—	—	—	3·5	—	—
26	2·2 (0·8)	2·4	0·9	—	4·2	4·0§	—
27	—	—	—	—	3·8	—	—
28	1·0	1·1	7·7	—	3·6	1·4§	—
29	—	—	—	—	3·6	—	—
30	0·5	0·6	37·8†	—	2·0	0·6§	—
31	—	—	—	—	2·2	—	—
32	—	—	19·0†	—	0·4	—	—
33	—	—	—	—	0·5	—	—
34	—	—	1·5	—	—	—	—
iso-12	0·3 (0·4)	Trace	—	—	—	—	—
14	4·1 (2·8)	2·5	—	0·5	Trace	—	—
16	6·7 (5·8)	6·4	—	1·4	0·2	0·1	0·3
18	4·5 (4·0)	5·4	—	24·3‡	0·4	0·4	17·0‖
20	5·2 (5·0)	6·3	—	3·2	0·2	7·0§	11·8‖
22	2·4 (4·0)	2·7	—	3·6	3·2	4·0§	16·2‖
24	3·2 (2·8)	3·8	—	5·8	4·6	5·0§	10·2‖
26	5·2 (3·6)	5·8	—	—	7·0	14·3§	0·1
28	2·2 (0·8)	2·6	—	—	5·2	5·0	—
30	1·3	1·6	3·4	—	1·6	—	—
32	—	1·1	4·6	—	0·9	—	—

* Figures in brackets are wt. % of acids isolated by Weitkamp (1945) who also found *n*-C_{10} (0·3%), *iso*-C_{10} (0·1%), *anteiso*-C_9 (0·1%), and *anteiso*-C_{11} (0·6%) acids.

† Acids isolated by Horn and Pretorius (1956).

‡ Acids isolated by Horn *et al.* (1954).

§ Alcohols isolated by Murray and Schoenfeld (1952, 1955).

‖ Diols isolated by Horn and Hougen (1953).

TABLE 4 (*Continued*)

Hydrocarbon Series Carbon Number	Non-Hydroxylated Acids		ω-Hydroxy Acids	α-Hydroxy Acids	Naturally Occurring Hydrocarbons	Monohydric Alcohols	α,β-Diols
	Via Iodides	Via Tosylates					
anteiso-13	1·1 (1·0)*	0·5	—	Trace	—	—	—
15	7·7 (4·8)	5·9	—	1·1	0·1	—	0·1
17	4·1 (3·6)	4·1	—	0·4	0·7	0·1§	0·6
19	6·3 (4·8)	6·2	—	3·1	0·3	0·3§§	5·8
21	5·8 (5·6)	6·1	—	2·4	0·4	3·8§	12·3
23	3·2 (3·6)	3·0	—	5·2	0·8	1·8§	15·0
25	6·2 (7·0)	7·1	—	2·7	2·2	8·4§	4·1
27	5·5 (5·2)	6·8	0·5	—	3·1	18·1§	—
29	3·9	3·6	4·6	—	1·0	6·3	—
31	2·6 (1·0)	2·6	12·3	—	—	2·3	—
33	—	2·0	7·7	—	—	1·5	—

* Figures in brackets are wt. % of acids isolated by Weitkamp (1945) who also found *n*-C_{16} (0·3%), *iso*-C_{19} (0·1%), *anteiso*-C_9 (0·1%), and *anteiso*-C_{11} (0·6%) acids.

§ Alcohols isolated by Murray and Schoenfeld (1952, 1955).

(1945) by low-pressure amplified-distillation of the methyl esters was able to report such an analysis for the non-hydroxylated acids. Weitkamp's figures are largely substantiated by the present work, although four of the lowest boiling constituents reported by him were not detected and six additional compounds of high carbon number have been shown to be present.

Horn and Pretorius (1956) reported the presence of an ω-hydroxy acid fraction, of which the normal C_{30} and C_{32} acids formed 50 and 30 per cent. respectively. They obtained evidence for a C_{31} component and for acids of lower molecular weight. The present work shows that the C_{30} and C_{32} compounds are the major constituents of a series of even carbon numbered normal ω-hydroxy acids from C_{26} to C_{34}, accompanied by smaller amounts of even-carbon *iso*- and odd-carbon *anteiso*-compounds. The principal branched acid is a C_{31} *anteiso*-compound and probably is the acid noted by Horn and Pretorius (1956). The isolation of these branched-chain hydroxy acids is in progress to determine the position of the hydroxyl group.

Horn *et al.* (1954) isolated from wool wax normal C_{12}, C_{14}, C_{16}, and C_{18} α-hydroxy acids and the *iso*-C_{18} α-hydroxy acid. These correspond to the major constituents of the hydrocarbon mixture examined above, except that the C_{12} member was not found. The hydrocarbon mixture also contained smaller quantities of additional odd- and even-carbon normal compounds from C_{14} to C_{24}, *anteiso*-compounds from C_{15} to C_{25}, and *iso*-compounds from C_{14} to C_{24}. The striking feature of the α-hydroxy acid fraction is the preponderance of the normal C_{16} and *iso* C_{18} components, which together constitute more than 60 per cent.

From the monohydric alcohols, Murray and Schoenfeld (1955) identified seven normal alcohols of even carbon number from C_{18} to C_{30}. These correspond to the normal compounds detected in the present work, in which a small amount of the C_{16} member was also found. In the *iso*- and *anteiso*-series six higher boiling and two lower boiling constituents are present in addition to the 10 branched-chain alcohols isolated earlier by Murray and Schoenfeld (1952).

During the fractionation of the unsaponifiable fraction the α,β-diols became divided into two parts, (i) those which did and (ii) those which did not form an adduct with urea. The two fractions were separately reduced to hydrocarbons and examined by gas chromatography, showing, as might be expected, that the longer-chain diols were more readily adducted. The composition of the hydrocarbon mixture from the α,β-diols in Table 4 was calculated from the combined figures for the two fractions. The normal compounds form only a small proportion of the mixture and the most abundant member of this series (C_{16}) has been identified by Horn and Hougen (1953). They also isolated the four major components of the *iso*-series but did not find any member of the series of *anteiso*-compounds found in the present work. No indication was obtained of the presence of α,ω-diols in the unsaponifiable fraction.

When the unsaponifiable fraction is chromatographed on alumina a small amount is eluted by light petroleum. Horn (1958) regarded this fraction as paraffin hydrocarbons but was unable to isolate any constituents by distillation. This fraction has now been found to contain non-urea adducting material which absorbs in the carbonyl and conjugated carbonyl regions of the infra-red spectrum. It is probable that this material consists of degradation products of sterols since it gives a Liebermann-Burchard colour similar to that of lanosterol. The fraction which was separable as a urea adduct had an infra-red spectrum of saturated hydrocarbons. This hydrocarbon mixture on analysis showed a preponderance of normal compounds which formed a complete homologous series from C_{13} to C_{33}. The branched-chain material consisted of *iso*- and *anteiso*-compounds as in each of the other wool-wax fractions. The mixture probably contained a considerable amount of higher molecular weight hydrocarbons which could not be eluted from the gas chromatograph and this conclusion is also suggested by the high melting point of the fraction.

It had been hoped that when a more complete picture had been obtained of the distribution of carbon number of the constituents in the various fractions of wool wax, some conclusion regarding the biosynthesis of the wax might be drawn. The results however are not particularly suggestive in this respect. The long-chain aliphatic alcohols in plant and insect waxes have long been supposed to have arisen by reduction of acids of the same carbon number (Chibnall and Piper 1934). If this occurs in the formation of wool wax some similarity between the corresponding acid and alcohol fractions would then be expected. As may be seen from the chromatograms, the monohydric alcohol and non-hydroxylated acid fractions, as well as the α,β-diol and the α-hydroxy acid fractions, have somewhat similar compositions above C_{20} but are quite different below this carbon number.

The fact that in all the acid and alcohol fractions the principal members of the normal series, and all members of the two branched series differ by two carbons suggests that chain extension has been by acetate addition (Rittenberg and Bloch 1944, 1945). However, the naturally occurring hydrocarbons, principally of the normal series, do not show this alternation of carbon number. Small quantities of odd carbon-numbered normal compounds are indicated, for the first time, as in animal fats (Hansen and McInnes 1954). Traces of odd carbon *iso*- and even carbon numbered *anteiso*-compounds could have been present but they would not have been resolved.

The examination of wax constituents by gas chromatography of the derived hydrocarbons was originally used to investigate the branched-chain acids of the tubercle bacillus wax (Kranz and Murray, unpublished data). However, the method found a more ready application to wool wax and other waxes are being similarly investigated in this laboratory. The use of the derived hydrocarbons has two desirable features: (i) Their stability and rapid elution permits the investigation of compounds with carbon numbers of C_{40} or more, much greater than would be possible with the methylated or acetylated derivatives; (ii) the only reference compounds needed are hydrocarbons, which are probably more readily available. When several classes of compounds are being investigated the reliability of the result depends on the clear-cut separation of the classes before reduction to hydrocarbons. In the present work care was taken that these separations were complete. A clear example of this is the separation of the α,β- and the α,ω-diols, obtained respectively from the α- and ω-hydroxy acids. The de ived hydrocarbon mixtures are totally different in composition, having not a single compound in common.

In the pa t the positive determination of the carbon number of long-chain wax constituents proved difficult until the means of separating them in high purity by precise fractional distillation was introduced, so that their physical properties (m.p., long crystal spacings) could be used for comparison with confidence. Separation and identification was a lengthy process so that the use of gas chromatography with its speed, its high resolving power, its accuracy, and the proof it affords of homology is a natural development in the investigation of waxes.

Confidence in the results of this work is maintained by the agreement with those of earlier wo kers using more classical methods. With a few exceptions the compounds previously reported have been indicated in the expected amounts. The analysis extends the knowledge of the composition of wool wax to constituents not access ble by these earlier methods.

IV. Acknowledgments

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THE SYNTHESIS OF 5,7–DICHLOROCOUMARAN–3–ONE AND RELATED PROBLEMS

By W. L. F. Armarego*

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Summary

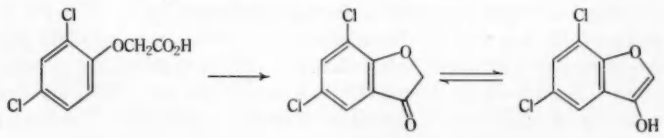
5,7-Dichlorocoumaran-3-one has been prepared from methyl 2-hydroxy-3,5-dichlorobenzoate by a three stage synthesis.

It could not be prepared by (i) intramolecular cyclization of 2,4-dichlorophenoxyacetic acid or 2,4-dichlorophenoxyacetyl chloride or (ii) by the reaction of ω-bromo-2-hydroxy-3,5-dichloroacetophenone with bases.

The reaction of 2,4-dichlorophenoxyacetic acid with phosphorus pentoxide in benzene gave 2,4-dichlorophenol, 2′,4′-dichlorophenyl 2,4-dichlorophenoxyacetate, and diphenylmethane. By the use of ^{14}C-labelled acids the methylene carbon atom of the diphenylmethane was shown to be derived from the methylene carbon atom of 2,4-dichlorophenoxyacetic acid. A possible mechanism is proposed for this reaction.

I. Introduction

Several reasons have been suggested for the plant growth activity of 2,4-dichlorophenoxyacetic acid. Detailed study of the biological activity of compounds related to this acid (Synerholm and Zimmerman 1945, 1947; Thompson *et al.* 1946) have indicated that the essential features for the activity are: (i) a phenoxy group with an alkane carboxylic acid side chain with an even number of carbon atoms, (ii) a carbonyl or potential carbonyl group β- to the ethereal linkage, (iii) at least one hydrogen on the carbon atom α- to the



(I) (II) (III)

ether link, and (iv) at least one unsubstituted position *ortho* to the ethereal oxygen. The latter was deduced from the fact that 2,6-disubstituted phenoxyacetic acids have negligible growth activity (Wain 1953). This led Rhodes and de Be Ashworth (1952) to postulate that 2,4-dichlorophenoxyacetic acid, for example, reacts to form the coumaranone (II) in the plant, and that the activity possibly depended on the tautomerism II⇌III. The present paper now describes the attempts made to synthesize the coumaranone (II).

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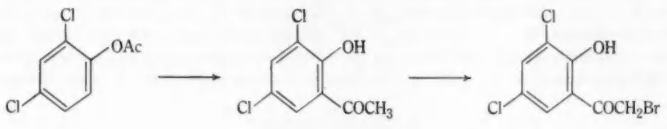
II. Results and Discussion

In the first attempt, an intramolecular Friedel-Crafts reaction with 2,4-dichlorophenoxyacetyl chloride was studied. The acid chloride reacted vigorously with anhydrous aluminium chloride and, when the reaction was carried out at low temperature without a solvent, a complex was formed which decomposed on warming to reform the acid chloride. On treatment with benzene the complex gave ω-2,4-dichlorophenoxyacetophenone. If on the other hand nitrobenzene was used as solvent 2′,4′-dichlorophenyl 2,4-dichlorophenoxyacetate was isolated. In both these reactions 2,4-dichlorophenol was also formed. Attempted cyclization of the acid chloride with stannic chloride or of the acid with polyphosphoric acid or 10 per cent. fuming sulphuric acid was unsuccessful.

The second route attempted for the preparation of 5,7-dichlorocoumaran-3-one was via ω-bromo-2-hydroxy-3,5-dichloroacetophenone (VI). 2,4-Dichlorophenol was acetylated and then made to undergo a Fries rearrangement (Sen and Bhargava 1949). The acetophenone (V) was acetylated and the resulting



(IV) (V) (VI)

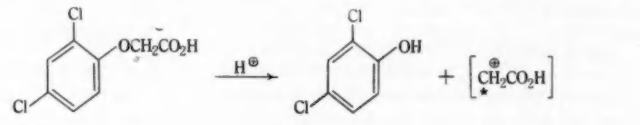
acetate brominated in carbon disulphide according to the method used by Duncanson *et al.* (1957) for preparing 2,6-diacetoxy-ω-bromo-4-methoxyacetophenone. The bromo compound was deacetylated to ω-bromo-2-hydroxy-3,5-dichloroacetophenone. As ω-halo-*o*-hydroxyacetophenones are readily converted to coumaran-3-ones when reacted with bases in ethanol (e.g. Shriner, Matson, and Damschroda 1939; Shriner and Witte 1939; Duncanson *et al.* 1957), this method was tried using the bromo compound (VI). The red product, which was isolated, was very soluble in all common solvents except light petroleum but it could not be purified by crystallization and it decomposed on attempted sublimation. It showed no characteristic bands in the ultraviolet spectrum and it gave bands at 1235 cm^{-1} (possibly ethereal), 1650 cm^{-1} (carbonyl), and 3400 cm^{-1} (possibly hydroxyl) in the infra-red. This red material was not investigated further as its properties differed from those expected for a coumaran-3-one.

Kalinowsky and Kalinowsky (1948) have made three unsuccessful attempts to synthesize 5,7-dichlorocoumaran-3-one. One of the methods was to react 2,4-dichlorophenoxyacetic acid with phosphorus pentoxide in anhydrous benzene and they isolated 2′,4′-dichlorophenyl 2,4-dichlorophenoxyacetate as the sole product. Since several coumaran-3-ones have been prepared from phenoxyacetic acids under these conditions (Stroemer and Bartsch 1900; Kalinowsky and Kalinowsky 1948) it was decided to investigate this reaction further with the dichloro acid using various reaction conditions in order to see if any 5,7-dichlorocoumaran-3-one could be obtained. The results of the abovementioned authors

were confirmed and no coumaranone was formed, even under the widely different conditions used. It was found that in addition to the above ester, 2,4-dichlorophenol and a substance b.p. 74 °C/0·4 mm were always formed. The yield of this last product was the same when 2 mol of phosphorus pentoxide were used per mol of acid and the reaction time kept between 1·5–2 hr. It was identified as diphenylmethane by elemental analysis, the absence of a C-methyl group, ultraviolet spectrum in comparison with an authentic specimen, oxidation to benzophenone, and characterization of the latter as its phenylhydrazone.

Since 2,4-dichlorophenoxyacetic acid is the source of this hydrocarbon then the phenyl groups must have originated from the solvent and the methylene carbon atom from the acid. The methylene carbon atom of the acid was the most likely source of the methylene carbon atom in the diphenylmethane. The reaction of (2,4-dichlorophenoxy)acetic 1-^{14}C acid and (2,4-dichlorophenoxy)acetic 2-^{14}C acid with phosphorus pentoxide in benzene was independently studied. It was found that the diphenylmethane isolated from the reaction with the acid labelled on the carboxyl group had no trace of radioactivity, whereas the diphenylmethane isolated from the reaction using the acid labelled on the methylene carbon atom possessed 25 per cent. of the radioactivity of the acid.

The mechanism probably involves the formation of formaldehyde (or its equivalent) which then reacts with the solvent. This is shown in the following scheme :



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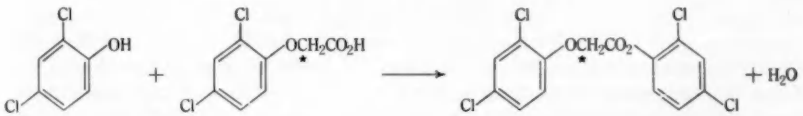

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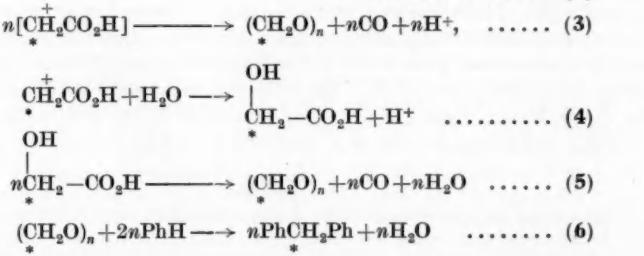


..... (3)

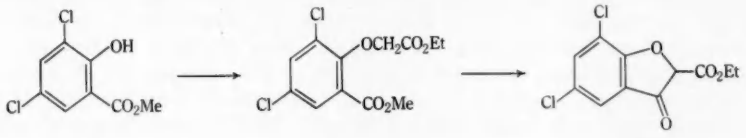
..... (4)

..... (5)

..... (6)

Scheme for the mechanism of the reaction of (2,4-dichlorophenoxy)acetic 2-^{14}C acid with phosphorus pentoxide in benzene.

The first two steps are straightforward. The carbonium ion formed in relation (1) decomposes to give formaldehyde or its polymer according to reaction (3) or alternatively it could react as in (4) and (5) through the intermediate glycollic acid also to give formaldehyde or its equivalent. That glycollic acid or formaldehyde are possible intermediates in the mechanism was shown by the isolation of diphenyl methane from the reactions of either glycollic acid or formaldehyde with benzene in the presence of phosphorus pentoxide. The formaldehyde then reacts with the solvent to form diphenyl methane as in (6). Only 58 per cent. of the radioactivity in the reaction of the acid labelled on the methylene carbon atom could be accounted for and, since 2,4-dichlorophenol was isolated, then the radioactivity unaccounted for must have been lost as formaldehyde. In the reaction with the carboxyl labelled acid only 33 per cent. of the radioactivity was accounted for, hence the rest of the radioactivity must have been lost as radioactive carbon monoxide.



(VII) (VIII) (IX)

5,7-Dichlorocoumaran-3-one was finally synthesized by an unambiguous method starting from salicylic acid which was first chlorinated to 2-hydroxy-3,5-dichlorobenzoic acid (Earle and Jackson 1906). This was converted to the acid chloride in high yield, using thionyl chloride, and then esterified. The methyl ester (VII) was condensed with ethyl bromoacetate in acetone to give ethyl 2,4-dichloro-6-methoxycarbonylphenoxyacetate (VIII). Intramolecular cyclization of this ester in benzene over sodium gave ethoxycarbonyl 5,7-dichlorocoumaran-3-one (IX). Emmott and Livingstone (1958) have shown that the hydrolysis and decarboxylation of 4-oxo-5-ethoxycarbonylnaphtho(2′,3′,2,3-)furan was best achieved by heating a solution of the ester in alcohol with 30 per cent. sodium hydroxide for not more than 0·5 hr. By using this method, 5,7-dichlorocoumaran-3-one (III) was obtained in 83 per cent. yield from IX. It was pale yellow when pure and a solution in ethanol, when allowed to stand at room temperature for a day, turned deep red. Evaporation of the alcoholic solution gave a red solid which did not appear to be different from the red solid obtained from compound VI. The coumaranone displayed keto-enol tautomerism as shown by (i) violet colouration produced with ferric chloride, (ii) formation of a 2,4-dinitrophenylhydrazone, and (iii) an acetyl derivative.

III. Experimental

All melting points are uncorrected. Light petroleum (b.p. 40–60 °C) was used. Whatman No. 1 chromatographic paper was used.

(*a*) *Friedel-Crafts Reaction on 2,4-Dichlorophenoxyacetyl Chloride.*—(i) *In Benzene.* When the acid chloride (redistilled b.p. 120 °C/2·0 mm, 12·0 g) was cooled to —50 °C in an ethanol/solid carbon dioxide bath, and powdered anhydrous aluminium chloride (7·3 g, 50% excess) was

added, with thorough stirring, the mixture turned to a deep red paste. The bath temperature was kept between —50 and —30 °C. Anhydrous benzene (25 ml) was added and the temperature was kept as low as possible. After standing at 0 °C for 0·5 hr the mixture was allowed to warm to room temperature and then refluxed for 0·5 hr. The solution was poured into ice-cold water, extracted with ether, and the ethereal layer was washed and dried (Na_2SO_4). The solvent was distilled off and the oily residue distilled under reduced pressure. The first fraction contained 2,4-dichlorophenol and the second fraction (b.p. 250–254 °C/18 mm) crystallized on cooling. ω-2,4-Dichlorophenoxyacetophenone crystallized from dilute methanol in colourless needles, m.p. 73·5–74·5 °C. Yield (2·8 g) 20% (Found: C, 60·1; H, 3·7; O, 11·5%. Calc. for $C_{14}H_{10}O_2Cl_2$: C, 59·8; H, 3·6; O, 11·4%).

(ii) *In Nitrobenzene.* The acid chloride (10·3 g) in redistilled nitrobenzene (20 ml) was treated with anhydrous aluminium chloride (6·5 g; 20% excess). Vigorous evolution of hydrogen chloride took place and the mixture was allowed to stand at room temperature for 18 hr. The solution was poured into ice-cold N hydrochloric acid (200 ml) and then steam distilled to remove the nitrobenzene. Some 2,4-dichlorophenol could be detected in the distillate. The pasty residue was extracted with ether, washed, and dried ($CaCl_2$). After removal of the solvent the residual oil was distilled. The fraction, b.p. 216 °C/0·7 mm, crystallized on standing. Yield (2·4 g) 31%. It crystallized in colourless needles, m.p. 112–113 °C (lit. 112–113 °C) (methanol or ethanol); m.p. and mixed m.p. with an authentic specimen of 2′,4′-dichlorophenyl 2,4-dichlorophenoxyacetate, 112–113 °C (methanol) (Found: C, 46·1; H, 2·6; Cl, 38·5%. Calc. for $C_{14}H_8O_3Cl_4$: C, 45·9; H, 2·2; Cl, 38·8%).

(*b*) *ω-Bromo-2-hydroxy-3,5-dichloroacetophenone.*—2-Acetoxy-3,5-dichloroacetophenone (20 g, in 94% yield from 2-hydroxy-3,5-dichloroacetophenone with acetic anhydride–perchloric acid) was dissolved in carbon disulphide (100 ml) and stirred. A solution of bromine (6·0 ml; 40% excess) in carbon disulphide (75 ml) was added at such a rate that the solution was decolorized before the addition of more bromine solution (1·5 hr). After standing (2 hr) the solvent was evaporated under reduced pressure and the residue solidified to a crystalline mass. *ω-Bromo-2-acetoxy-3,5-dichloroacetophenone* crystallized in pale yellow needles (light petroleum), m.p. 57–58 °C. Yield (20 g) 77% (Found: O. 14·6%. Calc. for $C_{10}H_7O_3Cl_2Br$: O, 14·7%).

Aqueous hydrobromic acid (100 ml; 48%) was added to a boiling solution of the above bromoacetate (14 g) in ethanol (240 ml) and the mixture boiled for 1 min and then diluted with hot water (100 ml). The solution was refluxed for another 20 min, diluted further with cold water (100 ml), and evaporated at room temperature. After the alcohol was removed, the oily layer solidified. The *ω-bromo-2-hydroxy-3,5-dichloroacetophenone* was filtered off and crystallized, yellow needles (light petroleum), m.p. 102–103 °C (Found: C, 34·1; H, 2·0; O, 11·4%. Calc. for $C_8H_5O_2Cl_2Br$: C, 33·9; H, 1·8; O, 11·3%).

(*c*) *Attempted Preparation of 5,7-Dichlorocoumaran-3-one.*—ω Bromo-2-hydroxy-3,5-dichloroacetophenone (7·7 g) was dissolved in ethanol (300 ml) and refluxed (1 hr) with a solution of sodium acetate trihydrate (7·7 g) in ethanol (300 ml). After warming for a few minutes, the colour of the solution was deep red. Evaporation to dryness gave a deep red solid which was dissolved in ether and washed thoroughly with water. The colour could not be extracted with acid but could be slowly extracted with dilute bases (NaOH, $NaHCO_3$). The ethereal layer was dried (Na_2SO_4) and evaporated to dryness (yield 4·9 g). This substance was soluble in all common organic solvents and could not be crystallized. It was strongly adsorbed on alumina and moved as a single red band on a cellulose column when eluted with *n*-butanol : acetic acid : water system (4 : 1 : 5). After two precipitations from benzene with light petroleum it had m.p. 155–170 °C (decomp.) (Found: C, 47·5; H, 2·0; O, 15·0%. Calc. for $C_8H_4O_2Cl_2$(5,7-dichlorocoumaran-3-one): C, 47·3; H, 2·0; O, 15·8%).

(*d*) *Methyl 2-Hydroxy-3,5-dichlorobenzoate.*—2-Hydroxy-3,5-dichlorobenzoic acid (49 g) was treated with excess thionyl chloride (50 ml) and boiled under reflux for 1·5 hr. Excess thionyl chloride was distilled off and the residual pale yellow crystalline solid dissolved in benzene (120 ml, Na dried) and carefully treated with methanol (150 ml). The solution was refluxed (0·5 hr) and cooled. The solid was isolated and crystallized as colourless needles from benzene/light petroleum, m.p. 148–149 °C (lit. 147 °C). Yield (40 g) 77% (Found: C, 43·1; H, 2·8%. Calc. for $C_8H_6O_3Cl_2$: C, 43·5; H, 2·7%).

(*e*) *Ethyl 2,4-Dichloro-6-methoxycarbonylphenoxyacetate.*—The above ester (22·1 g) was dissolved in the smallest volume of dry acetone (200 ml), and refluxed for 6 hr with ethyl bromoacetate (12·1 ml ; 10% excess) and anhydrous potassium carbonate (50 g). The acetone solution was filtered from the inorganic salts and the acetone distilled off. The residue was dissolved in ether, extracted with 10% sodium hydroxide then water, and dried ($CaCl_2$). The ether was distilled off and the *ester* crystallized in needles)(light petroleum), m.p. 63–64 °C. Yield (23·9 g) 78% (Found : C, 47·0 ; H, 4·0 ; Cl, 23·1%. Calc. for $C_{12}H_{12}O_5Cl_2$: C, 46·9 ; H, 3·9 ; Cl, 23·1%).

(*f*) *2-Ethoxycarbonyl-5,7-dichlorocoumaran-3-one.*—Freshly cut sodium (3·0 g) was added to a solution of the preceding ester (22·0 g) in benzene (100 ml ; Na dried) containing ethanol and the mixture refluxed for 3 hr. The benzene solution was decanted off from the residue and thoroughly extracted with water. The aqueous extract was diluted to 400 ml and carefully added to the residue. After the sodium had reacted completely this solution was acidified and the white precipitate formed was filtered off and dried. *2-Ethoxycarbonyl-5,7-dichlorocoumaran-3-one* crystallized in long white needles (ethanol), m.p. 180–181 °C, and gave a violet colour with ferric chloride. Yield (12·0 g) 60% (Found : C, 47·9 ; H, 3·0%. Calc. for $C_{11}H_8O_4Cl_2$: C, 48·0 ; H, 2·9%).

(*g*) *5,7-Dichlorocoumaran-3-one.*—The above ester (9·0 g) was suspended in ethanol (100 ml) and aqueous sodium hydroxide (150 ml ; 30%) added to the mixture. A clear yellow solution resulted after boiling for 5 min, but on further heating a white solid separated. The heating was continued for a total of 0·5 hr and the mixture poured into ice-cold water. This was acidified with hydrochloric acid and the precipitate filtered off, washed with water, and dried. *5,7-Dichlorocoumaran-3-one* was first crystallized from glacial acetic acid, sublimed (100 °C/0·7 mm), and then crystallized from ethanol : pale yellow needles, m.p. 134–135 °C (Found : C, 47·6 ; H, 2·2%. Calc. for $C_8H_4O_2Cl_2$: C, 47·3 ; H, 2·0%). It was soluble in sodium hydroxide and gave a violet colouration with ferric chloride. The *2,4-dinitrophenylhydrazone* crystallized as orange prisms (nitrobenzene), m.p. 225–226 °C (decomp.) (Found : C, 44·3 ; H, 2·2%. Calc. for $C_{14}H_8O_5N_4Cl_2$: C, 43·9 ; H, 2·1%). *3-Acetoxy-5,7-dichlorobenzofuran* was obtained in 75% yield by boiling with acetic anhydride for 2 hr. It crystallized in pale yellow needles (methanol), m.p. 109–110 °C (Found : C, 49·1 ; H, 2·8%. Calc. for $C_{10}H_6O_3Cl_2$: C, 49·0 ; H, 2·5%).

(*h*) *Reaction of 2,4-Dichlorophenoxyacetic Acid with Phosphorus Pentoxide in Benzene.*—The acid (50 g) was dissolved in boiling benzene (700 ml, Na dried) and treated with phosphorus pentoxide (66·6 g). After refluxing (1·5 hr) it was filtered and the residue extracted with boiling benzene (3 × 75 ml). The extracts were combined, added to the filtrate, extracted with 2N hydrochloric acid, saturated sodium bicarbonate then water, and dried (Na_2SO_4). Evaporation of the solvent gave a residue which partially crystallized on standing. The pasty solid crystallized from methanol as needles. Yield 16·6 g. On concentration a second crop (7·4 g) was obtained. These two crops (yield 58%) were combined and recrystallized from methanol ; m.p. and mixed m.p. with an authentic sample of 2′,4′-dichlorophenyl 2,4-dichlorophenoxyacetate was 112–113 °C (Found : C, 45·8 ; H, 2·4 ; Cl, 38·9%. Calc. for $C_{14}H_8O_3Cl_4$: C, 45·9 ; H, 2·2 ; Cl, 38·5%). The mother liquor from the first crystallization gave 2,4-dichlorophenol and an oil (7·5 g, 20%) b.p. 74 °C/0·4 mm (260·5 °C/764·5 nm). The latter crystallized on cooling, m.p. 24–25 °C (Found : C, 92·7 ; H, 7·2% ; C-Me, Nil. Calc. for $C_{13}H_{12}$: C, 92·8 ; H, 7·2% ; C-Me, Nil).

The ultraviolet spectrum was identical with that of diphenylmethane. The oil (2·05 g) was refluxed with aqueous potassium permanganate (4·0 g ; 40 ml water) for 6 hr. Benzophenone was isolated from this reaction, m.p. 47–48 °C (lit. 49 °C). Yield 1·32 g. The phenyl hydrazone had m.p. and mixed m.p. with an authentic specimen, 136–137 °C.

(*i*) *Reaction of Formaldehyde and Glycollic Acid with Phosphorus Pentoxide in Benzene.*—A 36% w/w solution of formaldehyde (15·0 ml) was shaken with benzene (150 ml, A.R.), and the benzene layer was refluxed with phosphorus pentoxide (40 g) for 1·5 hr. The benzene solution was treated as above and the residual oil (385 mg) distilled at 260–263 °C/760 mm, m.p. 23–25 °C, and was identified as diphenyl methane. Diphenyl methane was also isolated when glycollic acid was used in place of formaldehyde.

(*j*) *Reactions with Radioactive 2,4-Dichlorophenoxyacetic Acid.*—(i) *Method.* A known volume of a benzene solution of the radioactive acid was spotted on paper and run in *n*-butanol : ammonia : water system. The strip was then scanned on an automatic self-recording machine. The activity of the material per unit area could then be calculated by measuring the area under the peak obtained, since the total radioactivity of the material used is known. Any area thus obtained could be expressed directly in terms of specific activity. Although the other radioactive compounds isolated (diphenylmethane and 2′,4′-dichlorophenyl 2,4-dichlorophenoxyacetate) would have different absorption properties on the paper, different behaviour in the solvent system used, and different molecular weights, these differences are within the experimental errors. It can therefore be assumed that the areas under the recorded radioactive peaks are proportional to the specific activity of the substances.

The reaction of a definite amount of 2,4-dichlorophenoxyacetic acid, of known radioactivity, with phosphorus pentoxide in benzene was carried out and the acidic material, which was shown to contain radioactive 2,4-dichlorophenoxyacetic acid (unreacted) and 2,4-dichlorophenol, was separated from the reaction products. The radioactivity in the recovered acid (expressed in terms of area) was subtracted from the radioactivity in the original acid, thus giving the amount of radioactive acid that had reacted. The neutral products (2′,4′-dichlorophenyl 2,4-dichlorophenoxyacetate and diphenylmethane) were dissolved in a known volume of ethanol and an aliquot was spotted on paper and run in the abovementioned solvent system. In view of the high boiling point of diphenyl methane the amount lost by evaporation from the paper was well within the order of experimental error. By scanning the chromatogram and measuring the area under the peak (only one spot was obtained, R_F 0·91) the radioactivity of the neutral fraction was determined. This reaction was carried out with the carboxyl-labelled and methylene-labelled acids and the radioactivity of the neutral fractions compared.

The reactions were repeated and the neutral fraction was diluted with a known amount of non-labelled diphenyl methane. The diphenyl methane was freed from the ester by chromatography on alumina and after distillation, an aliquot was run on paper. The radioactivity of the diphenylmethane formed in the reaction was calculated from the area under the peak obtained.

(ii) *Results :* I (*a*). (2,4-Dichlorophenoxy)acetic 1-^{14}C acid (26 mg; 940 mμc) was dissolved in pure, dry benzene (3·00 ml). When an aliquot (20 μl; 1/150th) was spotted on paper and run in *n*-butanol : ammonia : water (10 : 1 : 1), one radioactive spot was obtained (R_F, 0·66). After scanning and measuring the area under the peak the activity left in the solution (viz. 3·00 ml—20 μl) was equivalent to 1275 cm². Phosphorus pentoxide (148 mg) was added and the solution was refluxed for 1·5 hr. The acidic material from the reaction was spotted on paper and run in the above solvent system (one spot R_F, 0·66) and its radioactivity was equivalent to 33·5 cm². Hence the radioactivity of the acid that had reacted was equivalent to 1241 cm². A fraction of the neutral material isolated was spotted and also run in the above solvent system. It gave one spot (R_F, 0·91) and, after scanning, it was found that the total radioactivity of the neutral products was equivalent to 410 cm². Hence this material possessed 33% of the activity in the acid that had reacted.

I (*b*). The reaction of (2,4-dichlorophenoxy)acetic 2-^{14}C acid (26 mg; 1400 mμc) with phosphorus pentoxide (172 mg) in benzene (3·00 ml) was carried out as in I (*a*) and it was found that the neutral material had 58% of the radioactivity of the acid that had reacted.

If it is assumed that no radioactive diphenyl methane was formed in I (*a*) then the radioactivity was only due to the ester, and in case I (*b*) the amount of radioactive diphenylmethane formed would be (58—33%) 25%. This was confirmed by the following experiments :

II (*a*). The above reaction was repeated using 28 mg of (2,4-dichlorophenoxy)acetic 1-^{14}C acid (activity; 7·06 μc) and 140 mg of phosphorus pentoxide in benzene (3·00 ml–20 μl). After refluxing for 1·5 hr, the unreacted material was recovered and the neutral fraction diluted with non-labelled diphenyl methane (1·00 ml). This was placed on an alumina column (10×1 in.) and eluted with light petroleum. The hydrocarbon which was thus separated from the ester was distilled at atmospheric pressure. Some of this hydrocarbon was spotted on paper but it was not radioactive.

II (*b*). (2,4-Dichlorophenoxy)acetic 2-^{14}C acid (29·9 mg; 12·6 μc) was reacted with phosphorus pentoxide (135 mg) in benzene (3·00 ml–20 μl) as in II (*a*). The neutral extract in this case was diluted with 1·20 ml of non-labelled diphenylmethane before purification by chromatography and distillation. The radioactivity in the diphenylmethane isolated was 25% of the radioactivity of the acid that had reacted.

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CHEMISTRY OF POLYNUCLEAR COMPOUNDS

IV. THE REDUCTION OF POLYNUCLEAR QUINONES WITH CYCLOHEXYL-*p*-TOLUENE SULPHONATE

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[*Manuscript received July* 15, 1959]

Summary

In an investigation into the coking mechanism of coal, polynuclear quinones have been adopted as models. Using *cyclo*hexyl-*p*-toluene sulphonate the following quinones have been reduced to their parent hydrocarbons: dibenzanthrone, *iso*dibenzanthrone, pyranthrone, 4,10-dibromoanthanthrone, anthraquinone (and anthrone), 1,5-dimethoxyanthraquinone, and 1,8-dimethoxyanthraquinone. The reaction gave favourable yields compared with alternative methods, but had the advantage that substituent groups such as halogen and alkoxyl were unattacked. A mechanism is proposed involving complexing of *cyclo*hexyl cations with the quinones, followed by hydrogen-transfer via a resonance-stabilized cyclic transition state.

I. INTRODUCTION

As part of a programme aimed at elucidating the chemical reactions involved during the coking of coal, a study is in progress of the pyrolytic reactions and coking of a series of polynuclear quinones. Parts I, II, and III of this series (Durie, Lack, and Shannon 1957; Durie and Shannon 1958*a*, 1958*b*) described the structures, the electronic and vibrational absorption spectra, and the behaviour in concentrated sulphuric acid of some of these quinones. Preliminary pyrolytic and coking results (Brown, Brooks, and Shannon 1958) have shown that dibenzanthrone and some of its derivatives decompose within the temperature range 300–450 °C to form semi-cokes in a similar fashion to coal. During the decomposition of these quinones only about one-half of their quinonoid oxygen was lost and the remainder was retained as quinone groups within the semi-cokes. Consequently in attempts to elucidate the chemical structure of the latter, methods of reduction of quinones of high molecular weight to their respective parent polynuclear hydrocarbons have been examined. This paper discusses the novel reduction of some polynuclear quinones with *cyclo*hexyl-*p*-toluene sulphonate.

When pyranthrone and excess *cyclo*hexyl-*p*-toluene sulphonate were heated together at 140 °C the reaction mixture first went purple in colour and then a vigorous reaction occurred in which *cyclo*hexene was evolved. Working up disclosed that apart from polymeric material (mainly poly*cyclo*hexyls) the hydrocarbon pyranthrene was the main product. Better yields of pyranthrene, comparing favourably with those given by known alternative methods, were obtained when pyranthrone and *cyclo*hexyl-*p*-toluene sulphonate were heated in

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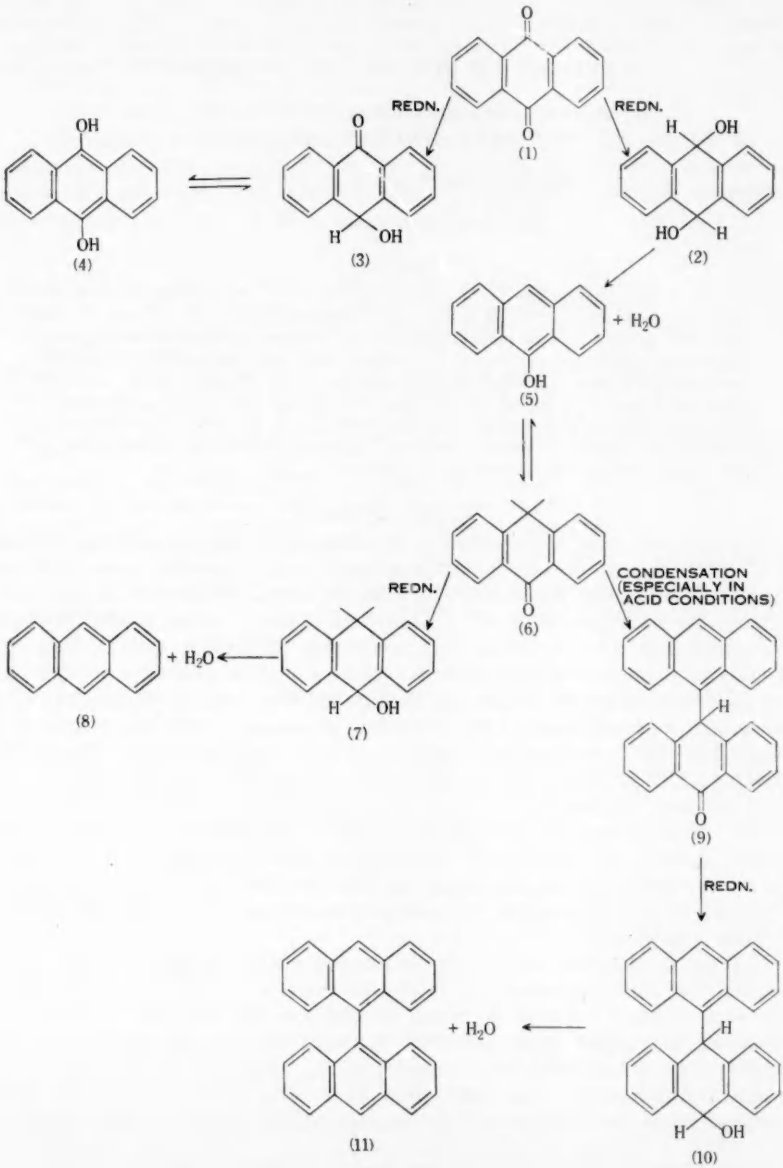

REDN.
REDN.
(1)
(2)
(3)
(4)
(5)
+ H_2O
CONDENSATION (ESPECIALLY IN ACID CONDITIONS)
REDN.
(6)
(7)
(8)
+ H_2O
(9)
REDN.
(10)
(11)
+ H_2O

trichlorobenzene as solvent. The addition of zinc dust to the reaction mixture further improved the method by decreasing the formation of the poly*cyclo*hexyls, thus facilitating isolation of the hydrocarbon product. In addition to pyranthrone the following quinones were reduced to their parent hydrocarbons: dibenzanthrone, *iso*dibenzanthrone, 4,10-dibromoanthanthrone, 1,5-dimethoxyanthraquinone, and 1,8-dimethoxyanthraquinone. Anthraquinone (and anthrone) were reduced to a mixture of anthracene and 9,9′-dianthryl.

II. Discussion

Steps in reduction of a typical polynuclear quinone, for example, anthraquinone, are depicted:

Although there are a variety of methods for producing the intermediate products, (2) to (7) (cf. Rodd 1956), reduction of a quinone to a hydrocarbon in a single step is restricted to a few methods, mostly using the reducing action of zinc dust and a variety of reagents, of which the following are examples: (*a*) ammonia; (*b*) acetic acid and pyridine (Clar 1948); (*c*) a melt of sodium chloride and zinc chloride (Clar 1939); (*d*) an acid or base in a melt of sodium chloride and aluminium chloride, following the procedure devised by Badische Anilin- und Soda-Fabrik (1954). Clar (1952) has suggested that in Method (*b*) the reaction proceeds via a pyridine-zinc acetate complex of the dihydroanthranol derivative (7). Method (*c*) gives varying amounts of the hydrocarbon (11) as well as of (8), depending upon the moisture content of the melt. It would appear that these zinc-dust methods would also reduce functional groups (halogen, hydroxyl, or alkoxyl) present in the molecule, though little has been published on the subject.

Another method of reducing a polynuclear quinone is due to Coffey and Boyd (1954), who studied the reduction of polycyclic quinones with aluminium alkoxides (Meerwein-Ponndorf reagent). These authors found that alkoxides of lower primary alcohols—for example, the ethoxide and *n*-butoxide—gave with anthraquinone only 9,10-dihydroxyanthracene (4), and therefore suggested that only one keto-group was reduced. When aluminium *iso*propoxide was used, however, both keto-groups were reduced and 9,10-dihydro-9,10-dihydroxyanthracene (2) was produced; further, with alkoxides of higher boiling alcohols—for example, butan-2-ol and *cyclo*hexanol—after 48 hr anthracene (8) was the main product. It may be that these latter conditions were sufficient to dehydrate (2) to (6), thus making available the anthrone keto-group for reduction. With chloro-substituted anthraquinones, Coffey and Boyd reported that reduction did not proceed past the chlorodihydroxy stage (2).

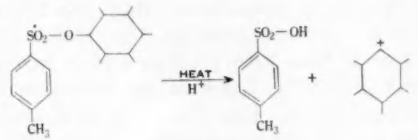
In the present method with *cyclo*hexyl-*p*-toluene sulphonate, reduction to the hydrocarbon is complete in less than half an hour, and with the examples investigated both halogen and methoxyl substituents remained unattacked. The following mechanism is suggested for the reduction with, for example, anthraquinone:

Step (*a*), which involves the proton-catalysed production of *cyclo*hexyl cations (initial protons presumably arising from trace amounts of free *p*-toluenesulphonic acid), has previously been suggested as the first step in the introduction

of *cyclo*hexyl groups into aromatic nuclei when *cyclo*hexyl-*p*-toluene sulphonate was heated with phenolic compounds at 120 °C (Hickinbottom and Rogers 1957). With quinones the deactivating nature of their carbonyl groups apparently inhibits this type of electrophilic substitution.

Step (*b*) is the addition of a *cyclo*hexyl cation on to each quinonoid oxygen atom. This is an analogous reaction to the well-known addition to quinones of aluminium halides and of protons from concentrated sulphuric acid. In fact, evidence for step (*b*) was provided by the similarity of the colours of the following quinones in concentrated sulphuric acid to the colours they gave in the first few minutes of reaction with *cyclo*hexyl-*p*-toluene sulphonate: dibenzanthrone, *iso*dibenzanthrone, 16,17-dimethoxydibenzanthrone, anthraquinone, acenaphthenequinone, and benzanthraquinone. Pyranthrone gave a purple colour in reaction with the *cyclo*hexyl ester whereas in sulphuric acid it was blue.

(*a*)



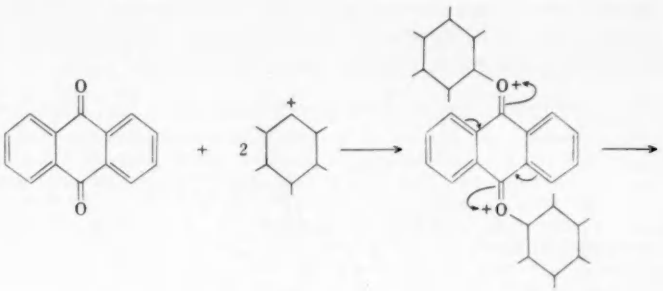
Some slight variations in these colours were not surprising, since it was known that different cations did not always complex with the same quinones to the same extent—for example, aluminium halides and concentrated sulphuric acid with anthraquinone (cf. Durie and Shannon 1958*a*). With all the quinones studied in this work, however, the intermediate coloured complexes formed in the reaction with the *cyclo*hexyl ester were observed visually; and with *iso*dibenzanthrone it was actually possible to measure the electronic absorption spectrum of the complex, which, as seen in Figure 1, resembles the spectrum obtained with concentrated sulphuric acid as the complexing agent. In other cases the lives of the quinone*cyclo*hexyl ester complexes were too short to permit spectroscopic measurement.

Step (*c*) involves the formation of a resonance-stabilized cyclic transition state the breakdown of which results in the hydrogen-transfer responsible for the reduction reaction. " Courtauld " models of the transition state have been constructed with anthraquinone and 1,8-dimethoxyanthraquinone. The latter may have been expected to be sterically hindered, but in both cases the hydrogen on the α-carbon atom of the *cyclo*hexyl group was situated favourably for resonance between it and the α-carbon atom of the quinone moiety.

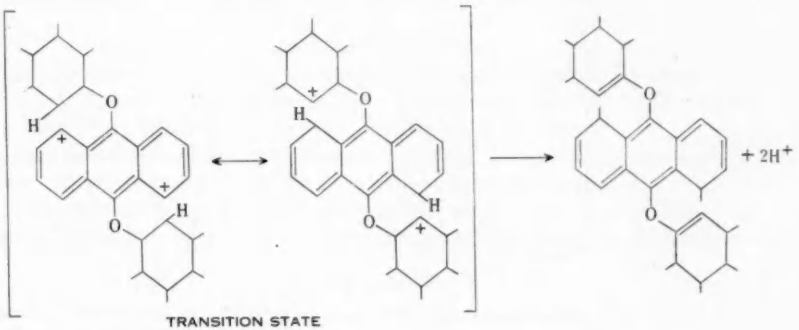
Resonance-stabilized cyclic transition states are known to be involved in other hydrogen-transfer reactions—for example, the Meerwein-Ponndorf reduction (Jackman and Mills 1949).

The breakdown of the newly proposed transition state in step (*c*) results in the formation of a vinyl-type ether which is known to be very readily hydrolysed under acid conditions (Rodd 1951), which of course prevailed in the present reaction. The resulting *cyclo*hexadiene was not isolated, but on the other hand it could be expected to polymerize under the conditions of the reaction. In

(*b*)



(*c*)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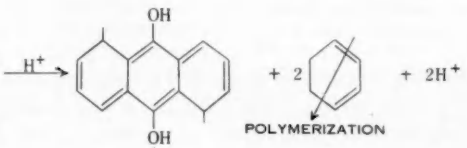
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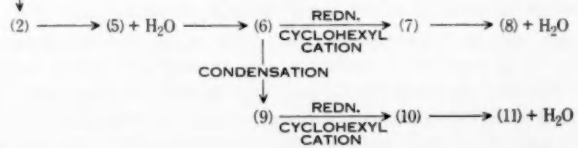
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CYCLOHEXYL CATION
CONDENSATION
REDN.
CYCLOHEXYL CATION

step (*c*) a proton lost from the other adjacent carbon atom would give an allyl ether. Although these do pyrolyse to diolefines, this requires a much higher temperature (about 300 °C) than that required for reduction (140 °C if no solvent is used). The rest of the steps are straightforward isomerizations and dehydrations. In regard to the latter, significant amounts of water were always present in the *cyclo*hexene fraction which distilled during the reaction.

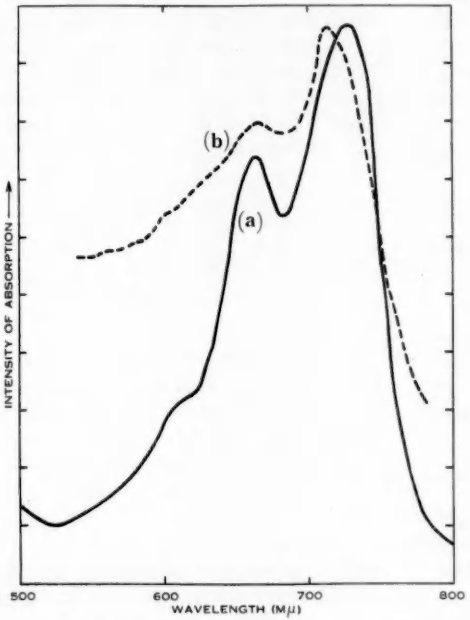

Fig. 1.—Absorption spectra of complexes of *iso*dibenzanthrone with (*a*) concentrated sulphuric acid and (*b*) *cyclo*hexyl cations.

It may be seen that the proposed mechanism proceeds via the formation of anthrone (6), which is in accord with the fact that anthracene and dianthryl were isolated as the main products from the reaction of anthrone with the *cyclo*hexyl ester.

Finally, since zinc dust in the presence of acids was known to reduce quinones, blank runs were carried out with several quinones, zinc dust, and *p*-toluenesulphonic acid in trichlorobenzene. Only with anthraquinone (and anthrone) were any hydrocarbons (anthracene and dianthryl) isolated, and even with these compounds the hydrocarbon yield was small. Furthermore, in all cases the reductions with the *cyclo*hexyl ester proceeded via the coloured complex with or without zinc dust, the main function of which was to lessen the formation of poly*cyclo*hexyls and thus facilitate isolation of the hydrocarbon product.

III. Experimental

The electronic spectra were measured on a Unicam SP500 spectrophotometer.

(*a*) Various experimental procedures were investigated, and the following description of the reduction of pyranthrone to pyranthrene represents typical optimum conditions: A mixture of pyranthrone (2 g) and zinc dust (15 g) in trichlorobenzene (30 ml) was heated under reflux in a 250 ml three-necked flask, fitted with a stirrer and a short air condenser which carried a take-off water condenser. A solution of *cyclo*hexyl-*p*-toluene sulphonate (40 g) in trichlorobenzene (70 ml) was added slowly to the solution, the operation occupying 15 min. When one-third of the ester had been added the mixture passed through a purple stage, a vigorous reaction occurred, and *cyclo*hexene and water distilled over. Heating was continued for a further 15 min after addition of the ester. The mixture was then cooled, extracted several times with water, and the trichlorobenzene layer dried and chromatographed on alumina at 140 °C with trichlorobenzene as eluant. The eluate was concentrated to give 1 g of pure pyranthrene (54%, m.p. 372–373 °C) (lit. 372–373 °C). Violanthrene, *iso*violanthrene, pyranthrene, anthracene, 9,9′-dianthryl, and 1,5-dimethoxy- and 1,8-dimethoxyanthracene were identified from their electronic spectra and from published melting points. 4,10-Dibromoanthanthrene crystallizes from chlorobenzene in yellow needles, m.p. 297–298 °C (Found: C, 61·3; H, 2·3%. Calc. for $C_{22}H_{10}Br_2$: C, 60·9; H, 2·3%). It dissolves in concentrated sulphuric acid with a reddish violet colour.

(*b*) The *cyclo*hexyl-*p*-toluene sulphonate was prepared from *p*-toluenesulphonic acid and *cyclo*hexanol according to the directions given by Hickinbottom and Rogers (1957).

IV. Acknowledgments

The authors are grateful for support and encouragement received from Mr. H. R. Brown, Officer-in-Charge, Coal Research Section, C.S.I.R.O., during the course of the researches and in the preparation of the paper.

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POLYUNSATURATED *ISO*BUTYLAMIDES RELATED TO CITRAL

By A. MEISTERS* and P. C. WAILES*

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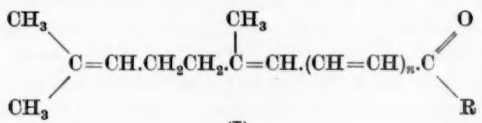
Summary

A group of polyunsaturated acids has been prepared from citral, and the *iso*-butylamides obtained from them have been tested for insecticidal activity. Two of the geometrical isomers of " citrylidene acetic acid " (I; $n=1$, R=OH), namely, the *trans*-2,*trans*-4 and *cis*-2,*cis*-4, have been obtained for the first time as crystalline solids.

I. INTRODUCTION

As a continuation of our study of amides designed to discover the structural features needed to confer high insecticidal activity (Wailes 1959), a group of compounds has been prepared of general formula I, where $n=0,1$, and 2 and R=H, OH, and $NHCH_2CH(CH_3)_2$.



(I)

The lack of insecticidal activity shown by the *iso*butylamides of the four stereoisomeric hexadeca-2,4-dienoic acids disclosed in our earlier work, together with the marked activity of affinin (II; $m=2$) and *neo*herculin (II; $m=3$) suggested that a necessary structural feature for high activity might be the interpolation of two methylene groups between centres of unsaturation.

$$CH_3\cdot(CH=CH)_m\cdot CH_2CH_2\cdot CH=CH\cdot CONHCH_2CH(CH_3)_2$$
(II)

Such an arrangement is present in citral (I; $n=0$, R=H) so by using citral as starting material and introducing more double bonds it has been possible to prepare several unsaturated *iso*butylamides which incorporate this structural feature. The effect of methyl groups as side chains could not be predicted but their close proximity to the double bonds must alter the molecular shape at these active centres and could therefore have an unfavourable effect on any insecticidal activity.

The source of the compounds was commercial citral from lemon grass oil which is known to contain up to 90 per cent. of *trans*-citral (the geometrical isomerism is relative to the longer chain).

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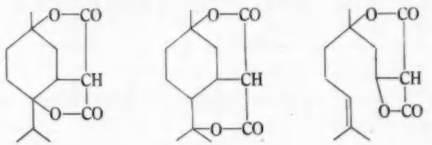
II. Discussion of Syntheses

(*a*) *Geranic Acid*

trans-Geranic acid (I; $n=0$, R=OH) was obtained by oxidation of citral with silver oxide in alkaline solution (Delépine and Bonnet 1909; Bernhauer and Forster 1936) followed by repeated distillation of the acid fraction to improve the absorption spectrum.

(*b*) *Citrylidene Acetic Acid* (*5,9-Dimethyldeca-2,4,8-trienoic Acid*)

This acid has been prepared by a variety of methods since it was first made by Verley (1899) from citral and malonic acid. In this reaction it was obtained as a by-product (see also Vul'fson and Shemyakin 1943), the main product being a dilactone for which Kuhn and Hoffer (1931) proposed formula III and Vul'f on and Shemyakin (1943) proposed formula IV.



(III) (IIIa) (IV)

The dilactone does not hydrogenate and is not attacked by ozone, both of which properties are satisfied by III, but conflict with IV. They are also satisfied by the alternative structure IIIa proposed by Kuhn and Hoffer but discarded by them in favour of III. Additional evidence to be described elsewhere (Hyne, Mole, and Wailes 1959) has led us to give preference to IIIa.

Above its melting point the dilactone loses carbon dioxide and is then converted into citrylidene acetic acid of unspecified configuration (Batty *et al.* 1937). The method of preparation of citrylidene acetic acid most used has been through use of a Reformatsky reaction with either citral or methyl heptenone

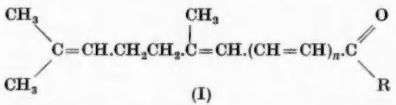
(V) (I; $n=1$, $R=OC_2H_5$)

(VIII) and the appropriate bromo ester (Tétry 1902; Royals 1947; van Dorp, Arens, and Inhoffen 1953; Samokhvalov *et al.* 1955; de Tribolet, Gamboni, and Schinz 1958). In addition it has been prepared from pseudo-ionone by the action of hypochlorite (de Tribolet and Schinz 1954) and some Russian workers have reported a rearrangement of the acetylenic malonic ester (V) to ethyl citrylidene acetate (Saricheva, Vorobyeva, and Preobrazhenskii 1957).

All the acids produced by these methods were oils of unspecified configurations whose ultraviolet absorptions (when reported) were quite low ($\varepsilon=10{,}000$

TABLE 1

PHYSICAL AND SPECTRAL DATA OF COMPOUNDS



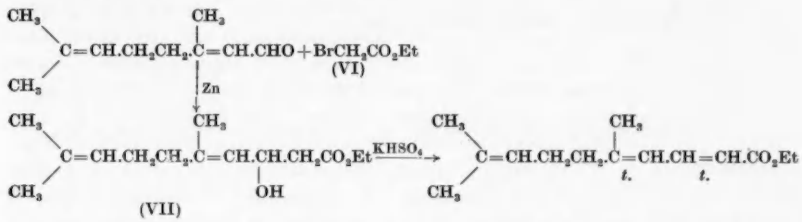
(I)

s, strong; m, medium; w, weak band; sh, shoulder; st, stretching; be, bending vibration
Infra-red as: * liquid film; † CCl_4 solution; ‡ Nujol mull; § see Section VI

Compound I	M.P. or B.P.	$\lambda_{max.}$ (mμ)	ε	n_D^{20}	C=O (st)	C=C (st)	=C—H (be) *t.*	C=C.COX *c.*	C=C.COX *t.*
Aldehydes, R=H									
n=1 (*t.-t.*)*	92 °C/0·2 mm	289·5	21,500	1·5326	1678s	1630s	1007w	—	884w
n=2 (all-*t.*)* ..	113–114 °C/0·2 mm	332	35,800	1·63§	1680s	1606s 1575w	967s 1008m 984s	—	886w
Acids, R=OH									
n=0 (*t.*)*	95 °C/0·1 mm	218	12,400	1·4872	1698s	1645s	930w	—	867w
n=1 (*t.-t.*)† ..	65–66 °C	273	27,900	—	1692s	1632s 1614s	982w 944w	—	887w
n=1 (*c.-c.*)† ..	52–53·5 °C	274·5	21,900	—	1694s	1628s 1596m	—	823m	—
n=2 (all-*t.*)† ..	86–88·5 °C	311	41,500	—	1690s	1637sh 1612s 1588m	1002s 944w	—	887w
n=2 (*t.-t.-c.*)† ..	50–53 °C	311	41,000	—	1690s	1638sh 1612s 1588m	1002s 944w	—	887w
*iso*Butylamides, R=NHCH$_2$CH(CH$_3$)$_2$									
n=0 (*t.*)*	120 °C/0·1 mm	221	13,800	1·4903	1638s	1667s	982w	—	—
n=1 (*t.-t.*)‡ ..	45–47 °C	273	32,600	—	1628s	1652m 1614m	985m	—	888w
n=1 (*c.-c.*)* ..	138 °C/0·1 mm	273·5	24,700	1·5263	1630s	1648s 1600m	—	815m	—
n=2 (all-*t.*)‡ ..	70–75 °C	307	45,900	—	1616s	1675m 1640w 1592w	998s 944w	—	885w

to 12,000). The work described here deals with the synthesis of two of the geometrical isomers of citrylidene acid as crystalline solids and the preparation of their *iso*butylamides.

(i) trans-trans-*Citrylidene Acetic Acid.*—A Reformatsky reaction between citral and ethyl bromoacetate (VI) followed by dehydration of the hydroxy ester (VII) with potassium bisulphate gave, as the main product, ethyl 5,9-dimethyldeca-*trans*-2,*trans*-4,8-trienoate (together no doubt with a small quantity of *trans*-2,*cis*-4-isomer from *cis*-citral):

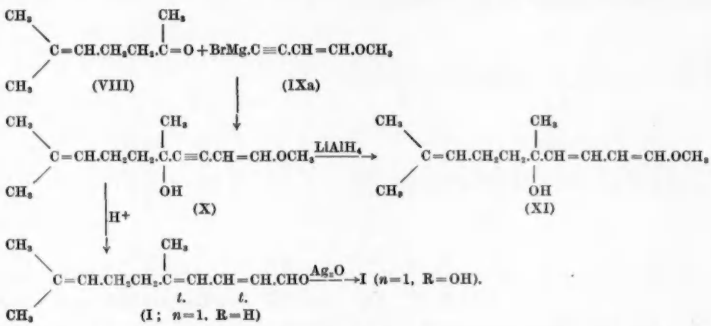


The extinction coefficient of the oily reaction product was of the order of 11,000 at the maximum (273 mμ). By repeated distillation this was raised to 15,000. On hydrolysis with alcoholic potassium hydroxide the acid was obtained as a viscous yellow oil which could not be crystallized. The acid was therefore converted to a solid derivative, the *S*-benzylthiouronium salt, which was crystallized twice and the free acid then liberated with dilute hydrochloric acid. The liberated acid was a colourless solid which could be crystallized readily from light petroleum as colourless needles. The frequencies of the main infra-red bands (Table 1) corresponded closely with those of straight chain *trans-trans*-2,4-dienoic acids and indicated that this was *trans-trans*-citrylidene acetic acid.

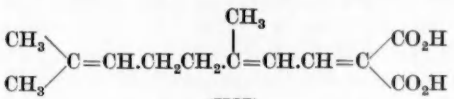
To confirm the geometrical configuration of the acid a second synthesis was carried out from methyl heptenone (VIII) and 1-methoxybut-1-en-3-yne (IX). This technique for chain extension by two *trans*-double bonds follows closely the method of Marshall and Whiting (1956). Commercial methyl heptenone (purified through its bisulphite compound) was condensed with methoxybutenynyl magnesium bromide (IXa) in tetrahydrofuran. The hydroxy ether (X) was liberated from its bromomagnesium salt with one equivalent of ethanol and then reduced to the *trans*-olefin (XI) by hydrogenation with lithium aluminium hydride. Finally, rearrangement with dilute acid afforded 5,9-dimethyldeca-*trans*-2,*trans*-4,8-trienal (I; $n=1$, R=H). Oxidation with silver oxide followed by low-temperature crystallization gave the crystalline *trans-trans*-citrylidene acetic acid identical in melting point (65–66 °C) and mixed melting point (undepressed) with the corresponding acid from the first synthesis.

(ii) cis-cis-*Citrylidene Acetic Acid.*—(1) *Condensation of Citral with Malonic Acid.* When citral was shaken with powdered malonic acid in pyridine the acid slowly dissolved to form a viscous orange coloured solution. After 3 days the unheated product was examined and 55 per cent. of the reaction product was found to be acidic and could be extracted from the neutral material with aqueous

potassium carbonate. Of the neutral fraction almost one-third was the dilactone, the remainder being made up of unreacted citral and by-products. The acidic fraction after 5 days showed an absorption maximum in the ultraviolet at 297 mμ (ε 10,900), the wavelength expected for a 2,4-diene-1,1-dioic acid. When the time was extended for a further period of several days at room temperature the crystalline dilactone slowly precipitated from the reaction medium. This process was accelerated if the crude acidic material was heated to about 100 °C



under reduced pressure when about 75 per cent. was rapidly converted into the solid dilactone (m.p. 189–190 °C). The crude acid gave a solid *S*-benzylthiouronium salt with $\lambda_{max.}$ 297·5 mμ (ε 21,900) from which 4,8-dimethylnona-1,3,7-triene-1,1-dicarboxylic acid (XII) was liberated as a yellow viscous oil with dilute hydrochloric acid, but it was unstable at room temperature, depositing the dilactone on standing. After several days the extinction coefficient at the maximum (297 mμ) had dropped to 17,600. The acid also formed a di-(*p*-bromophenacyl) ester which showed $\lambda_{max.}$ 258·5 and 288 mμ (ε 43,500, 29,900).

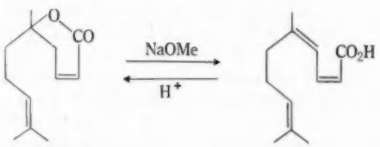


(XII)

(2) *Pyrolysis of the Dilactone.* The dilactone was heated at about 200 °C under reduced pressure with a little copper-bronze powder (Batty *et al.* 1937) then the pressure was reduced still further and the products distilled as a colourless oil. Extraction of this oil with potassium carbonate showed that only about one-third was a citrylidene acetic acid (I; n=1, R=OH); the remainder was neutral and showed a band at 1730 cm^{-1} indicating an αβ-unsaturated δ-lactone.

Acidic Fraction: On cooling over solid carbon dioxide for several days the acidic fraction solidified. It was crystallized from light petroleum at low temperatures and after several such crystallizations was obtained as colourless prisms, m.p. 52–53 °C, with an absorption maximum at 274·5 mμ (ε 21,900) typical of a conjugated dienoic acid. Its infra-red spectrum exhibited a medium band at 820 cm^{-1}. It now seems established that such a band is characteristic

of a *cis*-double bond conjugated with the carbonyl of an acid function (Allan, Meakins, and Whiting 1955 ; Crombie 1952 ; Sinclair *et al.* 1952). Assigning a configuration to the double bond at C_4 is more difficult. In their work on lycopene, Magoon and Zechmeister (1957) associate a band at 1380 cm^{-1} with trisubstituted *cis*-double bonds. In the case of the compound under discussion the interpretation is complicated by overlapping of the 1380 cm^{-1} band with the adjacent CH deformation band at 1385–1387 cm^{-1}. All that can be said with any certainty is that with this isomer of citrylidene acetic acid in carbon tetrachloride solution the 1380 cm^{-1} band predominates over the 1385–1387 cm^{-1} band while with the *trans-trans*-isomer the reverse applies. On this evidence, together with its origin from a cyclic compound and the close correspondence of C=C stretching frequencies with those of a *cis*-2,*cis*-4-acid, it is tentatively assigned this configuration. The acid lactonized very readily, a reaction which could be followed by infra-red analysis. The C=C stretching band at 1596 cm^{-1} gradually became weaker and a new band, characteristic of an αβ-unsaturated δ-lactone, appeared at 1725 cm^{-1}. If this lactone was freed of acid and treated with sodium methoxide in methanol the reformation of a 2,4-dienoic acid could be followed in the ultraviolet spectrum by observing the appearance of a band at 274 mμ. On isolation this acid was found to be identical with the original *cis-cis*-citrylidene acetic acid. The opening of a monosubstituted δ-lactone ring in this way gives a *cis*-2,*trans*-4-acid so if our configurational assignment is correct the presence of an additional, methyl, group at C_5 must have considerable influence on the course of the reaction.



(XIII)

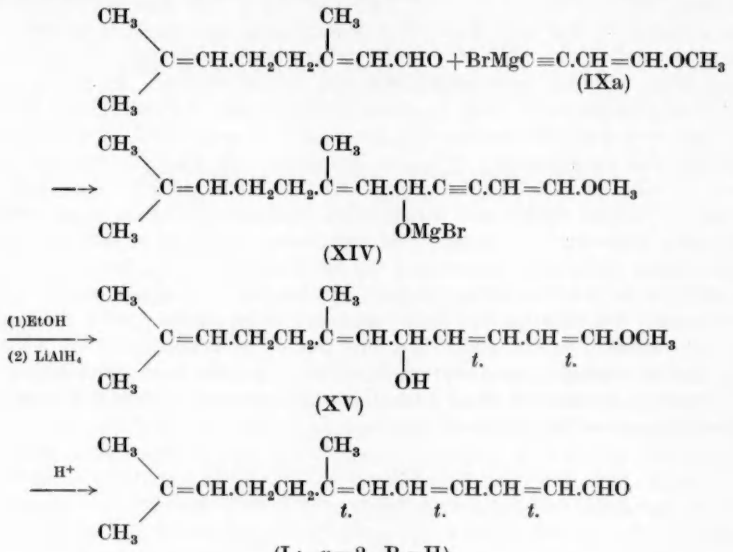
Lactone: The δ-lactone from the pyrolysis of the dilactone is probably of the same structure as XIII. On treatment with sodium methoxide in methanol this also forms the *cis*-2,*cis*-4-acid.

(*c*) *Citrylidene Crotonic Acid* (*7,11-Dimethyldodeca-2,4,6,10-tetraenoic Acid*)

The *trans*-2,*trans*-4,*trans*-6 isomer of this acid was obtained from citral by the chain extension method already used above with methyl heptenone. Citral was condensed with methoxybutenynyl magnesium bromide (IXa) and the intermediate bromomagnesium salt (XIV) was treated with ethanol (0·9 mol), lithium aluminium hydride, and then dilute acid. The resulting tetraenal (I ; $n=2$, R=H) was oxidized with silver oxide to the required all-*trans*-7,11-dimethyldodeca-2,4,6,10-tetraenoic acid.

Two forms of the acid were obtained, m.p. 50–53 °C and m.p. 86–88·5 °C. Their ultraviolet and infra-red spectra (Table 1) were almost identical, the latter differing only slightly in the 1380 cm^{-1} region, where, in carbon tetrachloride

solution, the acid of lower melting point exhibited a small prominent band which would seem to establish its configuration as *trans*-2,*trans*-4,*cis*-6 (Magoon and Zechmeister 1957). Both acids were extremely unstable in the solid state and, to a lesser extent, in solution. Polymerization was almost complete after 1 day at room temperature. Impure samples polymerized even more rapidly but the rate decreased with increasing purity.



(I; $n=2$, R=H).

III. Ultraviolet Absorption Spectra

All compounds showed a single broad maximum, the positions of which have been shifted by the presence of the methyl branch in the chromophore to wavelengths longer than those of the unbranched compounds, although the intensities have not changed. The relevant figures, all obtained in 95 per cent. ethanol on a Hilger Uvispek spectrophotometer, are set out in Table 1.

IV. Infra-Red Spectra

Table 1 shows the frequencies of the main peaks of the aldehydes, acids, and *iso*butylamides. They were obtained using a Perkin-Elmer Model 21 double-beam spectrometer with sodium chloride prism and are subject to the usual accuracy of this instrument. The methyl group at the end of the chromophores seems to make no difference to the absorption frequencies of C=O and C=C stretching vibrations since frequency values for these peaks are the same as those for corresponding non-branched compounds. The band previously noted at about 870 cm^{-1} with straight chain dienoic acids (Wailes 1959) and assigned to the grouping $-\underset{t.}{C}=C.COX$ is at slightly higher frequencies in the present series.

V. Insecticidal Activities

The *iso*butylamides of all acids were tested for insecticidal activity by Mr. R. W. Kerr of the Division of Entomology, C.S.I.R.O. They were applied in kerosene, or equal volumes of kerosene and acetone, to the thorax of male house-flies. *N-iso*Butyl-*trans-trans*-citrylidene acetamide applied as a 10 per cent. w/v solution at a rate of 770 μg/g body weight caused knockdown in 10 to 30 min, but not death since the flies recovered completely in 10 hr. (Affinin under similar conditions has LD 50, 20–27 μg/g.) The only other amide to show activity was *N-iso*butylgeranamide which at the very high dosage of 7000 μg/g body weight caused knockdown in 20 to 120 min from which the flies recovered in 12 hr but with permanent leg impairment. At dosages of 1400 μg/g and lower only minor effects were produced.

VI. Experimental

(*a*) *General*

Microanalyses were made by the C.S.I.R.O. and University of Melbourne Microanalytical Laboratory. Melting points were obtained on a Kofler heating stage microscope and are corrected. All distillations were carried out under nitrogen. Infra-red measurements were made by Mr. A. C. K. Triffett using a Perkin-Elmer Model 21 double-beam spectrometer with sodium chloride prism.

Preparation of iso*Butylamides : General Method.*—The acid was converted to the acyl chloride by warming for ½ hr in benzene with a slight excess of oxalyl chloride, after which the solvent was removed under reduced pressure, and the residue warmed under high vacuum to remove traces of oxalyl chloride. The acyl chloride was dissolved in dry ether, cooled in ice, and an excess of *iso*butylamine added slowly. After standing ½ hr at room temperature dilute sulphuric acid was added, the ethereal layer separated, washed, dried (Na_2SO_4), and evaporated. The *iso*butylamide, if a solid, was crystallized from light petroleum (b.p. <40 °C).

(*b*) *Geranic Acid*

Citral (10 g) was oxidized with silver oxide in aqueous alcoholic solution (after Bernhauer and Forster 1936) to give *trans*-geranic acid (6·5 g) which after two distillations had b.p. 95 °C/0·1 mm, n_D^{20} 1·4872, $\lambda_{max.}$ 218 mμ (ε 12,400). The *iso*butylamide had b.p. 120–121 °C/0·1 mm, n_D^{20} 1·4903, $\lambda_{max.}$ 221 mμ (ε 13,800) (Found : C, 75·1 ; H, 11·4 ; N, 6·4%. Calc. for $C_{14}H_{25}NO$: C, 75·3 ; H, 11·3 ; N, 6·3%).

(*c*) trans-trans-*Citrylidene Acetic Acid* (*5,9-Dimethyldeca*-trans-*2*,trans-*4,8-trienoic Acid*)

(*i*) *Ethyl 5,9-Dimethyldeca*-trans-*2*,trans-*4,8-trienoate.*—Zinc wool (12·1 g, washed with dilute hydrochloric acid, water, and acetone, then dried at 100 °C) was covered with tetrahydrofuran (30 ml), a few crystals of mercuric chloride were added, and the solvent brought to the boil. A mixture of redistilled citral (28·4 g) and ethyl bromoacetate (31·1 g) in tetrahydrofuran (20 ml) was then added with stirring at a rate sufficient to maintain gentle refluxing. After addition was complete (½ hr) refluxing was continued for 1 hr, after which the solution was cooled and 15% acetic acid added (200 ml) with stirring. The product was collected with ether, washed with water, and dried (Na_2SO_4). Evaporation of ether gave an oily residue which was mixed with powdered potassium bisulphate (20 g) and heated in an oil-bath to 160–170 °C at 100 mm pressure. Water elimination was complete at this temperature. After cooling the ester was extracted from the residue with ether and distilled to give a colourless oil in two main fractions : (1) 16·5 g, b.p. 97–101 °C/0·2 mm, n_D^{20} 1·5018, $\lambda_{max.}$ 275·5 mμ (ε 12,500) ; (2) 6·6 g, b.p. 101–105 °C/0·2 mm, n_D^{20} 1·5102, $\lambda_{max.}$ 275 mμ (ε 13,700). Both fractions showed the bands at 1614 and 1637 cm^{-1} associated with C=C stretching vibrations of a 2,4-dienoic ester, as well as the C=O peak at 1715 cm^{-1} ; but in addition absorption at 1735 cm^{-1} pointed to an unconjugated ester grouping. There was no evidence for a free hydroxyl group.

(ii) *5,9-Dimethyldeca*-trans-*2*,trans-*4,8-trienoic Acid.*—The material from fraction (1) above (13 g) was saponified with potassium hydroxide (3·6 g) in boiling methanol (31 ml) for ¾ hr under nitrogen. Distillation after isolation of the acidic fraction gave crude *trans-trans*-citrylidene acetic acid (8·7 g), b.p. 117–119 °C/0·1 mm, n_D^{20} 1·5334, as a yellow oil which could not be crystallized. Portion of the crude acid (0·36 g) was dissolved in potassium hydroxide solution and dilute hydrochloric acid added till neutral (phenolphthalein). *S*-Benzylthiouronium chloride (0·4 g) in water (10 ml) was added and after standing ½ hr the precipitated derivative was filtered off and crystallized from 50% aqueous ethanol several times to give small white prisms of the thiouronium salt (0·25 g), m.p. 135–136·5 °C (Found: C, 66·8; H, 8·0; N, 7·4%. Calc. for $C_{20}H_{28}N_2O_2S$: C, 66·6; H, 7·8; N, 7·8%). The derivative was shaken with 5N hydrochloric acid and the *trans-trans*-citrylidene acetic acid was liberated as a crystalline solid (0·14 g). Several crystallizations from light petroleum (b.p. <40 °C) gave the acid as colourless needles, m.p. 62·5–64·5 °C, $\lambda_{max.}$ 273 mμ (ε 27,700) (Found: C, 74·1; H, 9·5%. Calc. for $C_{12}H_{18}O_2$: C, 74·2; H, 9·2%). Preparation of the *iso*butylamide by the general method gave a mixture of two compounds, one melting at 95·5–97 °C and containing one atom of chlorine per molecule, the other melting at 45–47 °C and showing all the properties of the true *iso*butylamide. The chlorinated *iso*butylamide absorbed at slightly lower wavelength ($\lambda_{max.}$ 271·5 mμ, ε 32,100) in the ultraviolet and its infra-red spectrum was distinguished by bands at 1673, 1655, and 1612 cm^{-1} (Found: C, 67·7; H, 9·9; N, 4·8%. Calc. for $C_{16}H_{26}ClNO$: C, 67·7; H, 9·2; N, 4·9%). In other preparations this chlorinated amide was not isolated. The true *iso*butylamide had $\lambda_{max.}$ 273 mμ (ε 32,600) and infra-red bands in the normal positions (Table 1) (Found C, 77·1; H, 11·0; N, 5·9%. Calc. for $C_{16}H_{27}NO$: C, 77·1; H, 10·9; N, 5·6%).

(iii) *5,9-Dimethyldeca*-trans-*2*,trans-*4,8-trienal.*—1-Methoxybut-1-en-3-yne (4·5 g; 10% excess) in tetrahydrofuran (5 ml) was added dropwise to a stirred solution of ethyl magnesium bromide (from 1·2 g Mg) in tetrahydrofuran (40 ml), the mixture being maintained at about 40 °C. After stirring for 1 hr at room temperature, a solution of 2-methylhept-2-en-6-one (6·2 g) in tetrahydrofuran (5 ml) was added dropwise over 20 min with ice cooling. Stirring was continued at room temperature for 2 hr when (after cooling in ice) ethanol (2·6 ml; 90% of theory) was added followed after 20 min by lithium aluminium hydride (1·85 g). The mixture was stirred overnight then worked up by addition of ethyl acetate, saturated aqueous tartaric acid, and ether. The ether was separated, combined with further ether extracts of the aqueous layer, washed, evaporated, and distilled. The main fraction of the aldehyde (4·5 g) had b.p. 97–98 °C/0·2 mm, n_D^{20} 1·5326, $\lambda_{max.}$ 289·5 mμ (ε 21,500). The 2,4-dinitrophenylhydrazone melted over several degrees (145–150 °C) but analysed well (Found: C, 60·3; H, 6·1; N, 15·5%. Calc. for $C_{18}H_{22}N_4O_4$: C, 60·3; H, 6·2; N, 15·6%).

(iv) *Oxidation.*—To the trienal (3·5 g) in ethanol (50 ml) was added a solution of silver nitrate (5·1 g) in water (5 ml) and ethanol (200 ml). While passing nitrogen over the surface of the liquid and shaking, 5 ml of 10N sodium hydroxide solution diluted to 50 ml with ethanol was added over 15 min. The resultant black suspension was shaken for 20 hr, the solid filtered off, and the yellow solution freed of solvent under reduced pressure. The residue was taken up in water (80 ml), extracted six times with ether, then acidified, and the acid collected with ether. Crystallization from light petroleum (b.p. <40 °C) at low temperature gave white needles of *trans-trans*-citrylidene acetic acid (2·5 g), m.p. 65–66 °C, $\lambda_{max.}$ 273 (ε 27,900). A mixed m.p. with the acid prepared by the Reformatsky reaction was not depressed and infra-red spectra of both acids were identical.

(*d*) *5,9-Dimethyldeca*-cis-*2*,cis-*4,8-trienoic Acid*

(i) *Condensation of Citral with Malonic Acid.*—Citral (24 g), pyridine (12 ml), malonic acid (15 g), and piperidine (1 drop) were shaken together until all the malonic acid had dissolved (3 days). The pressure which had built up during the reaction was released and ether (125 ml) added to the orange coloured oil. The dilactone (4·0 g) which precipitated was collected by filtration (after removal of pyridine by shaking with dilute sulphuric acid) and the acidic material was extracted from the ethereal filtrate with potassium bicarbonate solution. Acidification of the alkaline extracts and extraction with ether gave the acidic fraction as a yellow oil (17·2 g).

The neutral fraction (10·6 g) was recovered from the alkali-extracted ethereal solution as a mobile yellow oil which showed the spectrum of citral and could not be solidified at —10 °C.

(ii) *4,8-Dimethylnona-1,3,7-triene-1,1-dicarboxylic Acid.*—Five days after isolation the acidic fraction showed an absorption maximum in the ultraviolet at 297 mμ (ε 10,900), and deposited the crystalline dilactone on standing. On heating the acidic material (4·75 g) to 100 °C at 70 mm pressure. the whole set solid within ½ hr. The solid, after extraction with ether, was shown to be pure dilactone (3·4 g), m.p. 186–190 °C, showing no absorption above 240 mμ. The di-(*S*-benzylthiouronium) salt of the acid was formed in rather poor yield and melted over a range ending at 99 °C but the absorption spectrum showed $\lambda_{max.}$ 297·5 mμ (ε 21,900). The dicarboxylic acid liberated from this derivative with dilute hydrochloric acid deposited the dilactone on standing The di-(*p*-bromophenacyl) ester crystallized well from aqueous ethanol as white prisms, m.p. 114·5–116·5 °C, and had $\lambda_{max.}$ 258·5 and 288 mμ (ε 43,500, 29,900) (Found : C, 55·0 ; H, 4·6 ; Br, 25·4%. Calc. for $C_{32}H_{36}Br_2O_6$: C, 55·1 ; H, 4·5 ; Br, 25·3%).

(iii) *Pyrolysis of the Dilactone.*—The solid dilactone (19·8 g) was intimately mixed with copper-bronze powder (0·1 g) and heated in a distillation flask to 200 °C under 50 mm pressure. After evolution of carbon dioxide had ceased (20 min) the pressure was reduced to 2 mm and the products distilled as a colourless oil (15·5 g). The distillate was dissolved in ether and separated into acidic (5·8 g) and neutral (9·7 g) components by extraction with potassium carbonate solution.

(iv) *5,9-Dimethyldeca-*cis*-2,*cis*-4,8-trienoic Acid.*—Distillation of the acidic material gave a main fraction (5·0 g), b.p. 140–142 °C/0·2 mm, n_D^{20} 1·5340, which solidified at —70 °C, and was crystallized several times from light petroleum at low temperatures to give colourless prisms, m.p. 52–53·5 °C, $\lambda_{max.}$ 274·5 mμ (ε 21,900) (Found : C, 74·0 ; H, 9·3%). Microhydrogenation required 3·1 H_2 and afforded 5,9-dimethyldecanoic acid which was identified as its *p*-bromophenacyl ester, m.p. 56–57 °C (Kuhn, Badstübner, and Grundmann (1936) give m.p. 56 °C) (Found : C, 60·6 ; H, 7·3 ; Br, 20·5%. Calc. for $C_{20}H_{29}BrO_3$: C, 60·5 ; H, 7·4 ; Br, 20·1%). As in the case of the *trans-trans*-isomer, preparation of the *iso*butylamide gave a mixture of the true *iso*butylamide, which was an oil at room temperature, b.p. 138 °C/0·1 mm, n_D^{20} 1·5263, $\lambda_{max.}$ 273·5 mμ (ε 24,700) (Found : C, 76·9 ; H, 11·2 ; N, 5·5%) and a chlorinated *iso*butylamide, m.p. 61–62·5 °C, $\lambda_{max.}$ 272 mμ (ε 26,000) (Found : C, 67·9 ; H, 9·8 ; N, 4·6 ; Cl, 13·5%. Calc. for $C_{16}H_{26}ClNO$: C, 67·7 ; H, 9·2 ; N, 4·9 ; Cl, 12·5%). The latter had infra-red bands at 1638, 1622, and 1604 cm^{-1}.

(v) *5,9-Dimethyldeca-2,8-dieno-5-lactone.*—The neutral fraction from the pyrolysis of the dilactone was distilled to give a colourless oil (9·2 g), b.p. 102–106 °C/0·2 mm, n_D^{20} 1·4842 (Found : C, 74·0 ; H, 9·4%. Calc. for $C_{12}H_{18}O_2$: C, 74·2 ; H, 9·3%). In the infra-red the compound exhibited a strong band at 1730 cm^{-1} characteristic of an αβ-unsaturated δ-lactone.

(vi) *Treatment with Sodium Methoxide.*—The monolactone above (3·0 g) was dissolved in a methanolic solution of sodium methoxide (from 0·4 g sodium in 32 ml of dry methanol) and set aside for 3 hr. The solvent was removed under reduced pressure and the residue was dissolved in water, extracted with ether to remove neutral material, then acidified and extracted again to obtain the acidic fraction. Distillation afforded 2·4 g of a colourless acid, b.p. 117–118 °C/0·1 mm, n_D^{20} 1·5297, which solidified on freezing. After several crystallizations from light petroleum the acid had m.p. 52–53·5 °C. A mixed m.p. with *cis-cis*-citrylidene acetic acid was not depressed.

(*e*) *all*-trans-*7,11-Dimethyldodeca-2,4,6,10-tetraenoic Acid*

(i) *7,11-Dimethyldodeca-2,4,6,10-tetraenal.*—1-Methoxybut-1-en-3-yne (10 g ; 30% excess) in tetrahydrofuran (10 ml) was added dropwise to a stirred solution of ethyl magnesium bromide (from 2·3 g Mg) in tetrahydrofuran (75 ml), the mixture being maintained at *c.* 40 °C. After 1 hr stirring at room temperature citral (14·4 g) in tetrahydrofuran (10 ml) was added dropwise over 20 min with ice cooling. The mixture was stirred for a further 1½ hr at 20 °C after which ethanol (4·8 ml ; 0·9 mol) was added, followed after 20 min with lithium aluminium hydride (3·6 g). After stirring overnight, ether and saturated aqueous tartaric acid were added with ice cooling. The aqueous suspension was extracted three times with ether, the extracts washed, dried

(Na_2SO_4), and evaporated. Distillation gave the aldehyde (13·5 g) as a yellow oil, b.p. 113–114 °C/0·2 mm, n_D^{20} 1·63 (obtained with a Leitz-Jelley refractometer), $\lambda_{max.}$ 332 mμ (ε 35,800) (Found: C, 82·2; H, 9·9%. Calc. for $C_{14}H_{20}O$: C, 82·3; H, 9·9%). The 2,4-dinitrophenylhydrazone was deep reddish brown in colour and had m.p. 142–144 °C (Found: C, 62·7; H, 6·4; N, 14·3%. Calc. for $C_{20}H_{24}N_4O_4$: C, 62·5; H, 6·3; N, 14·6%).

(ii) *7,11-Dimethyldodeca-2,4,6,11-tetraenoic Acid.*—The aldehyde (5·0 g) in ethanol (100 ml) was mixed with a solution of silver nitrate (6·35 g) in ethanol (200 ml) and water (5 ml) and sodium hydroxide solution (12·5 ml; 5N) diluted to 50 ml with ethanol was added under nitrogen over 15 min with shaking. The suspension was shaken at room temperature for 18 hr and worked up as for *trans-trans*-citrylidene acetic acid above. The tetraenoic acid was obtained as a pale yellow solid (4·5 g) which was separated by crystallization from light petroleum (b.p. <40 °C) into two compounds, a higher-melting all-*trans*-acid, m.p. 86–88·5 °C, $\lambda_{max.}$ 311 mμ (ε 41,500) (Found: C, 76·6; H, 9·2%. Calc. for $C_{14}H_{20}O_2$: C, 76·3; H, 9·1%) and a lower-melting form, m.p. 50–53 °C, which is discussed in Section II. It was extremely unstable, polymerizing much more readily than the all-*trans*-form, and was not investigated further. The *iso*butylamide of the all-*trans*-acid was obtained as white prisms, m.p. 70–75 °C, after several low-temperature crystallizations from light petroleum. Further crystallizations failed to reduce the melting range. The *iso*butylamide polymerized rapidly in the solid state but was reasonably stable in solution; it had $\lambda_{max.}$ 307 mμ (ε 45,900) (Found: C, 78·1; H, 10·8; N, 5·2%. Calc. for $C_{18}H_{29}NO$: C, 78·5; H, 10·6; N, 5·1%).

VII. Acknowledgments

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SYNTHESIS OF PENTANE-1,5-DIALDEHYDES*

By G. W. K. Cavill† and D. H. Solomon†

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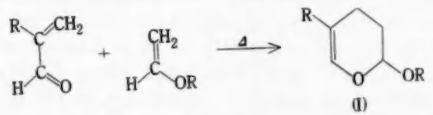
Summary

A general method for the synthesis of alkylpentane-1,5-dialdehydes is described. The appropriately substituted *cyclo*hexanone is oxidized with lead tetra-acetate in benzene solution, and the resultant 2,6-diacetoxy*cyclo*hexanone is reduced (lithium aluminium hydride) to the *cyclo*hexane-1,2,3-triol. Fission of the triol with sodium periodate yields the pentane-1,5-dialdehyde.

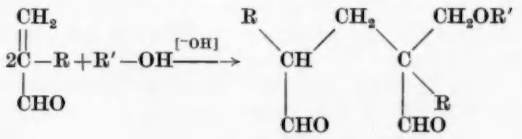
I. Introduction

Although 1,5-dialdehydes have been postulated as intermediates in the biosynthesis of natural products of plant and animal origin, for example, in the biosynthesis of pyridine and piperidine alkaloids (see Robinson 1955), few have been synthesized. Conversely, one of the few synthetic routes to alkylpentane-1,5-dialdehydes involves the degradation of the appropriate alkylpyridine, via the alkyldihydropyridine to the alkylpentane-1,5-dialdehyde dioxime (Shaw 1937); but the yield is poor (see Cope *et al.* 1951).



(I)

Industrially, glutardial and 2-methylglutardial are formed by acid hydrolysis of a 2-alkoxydihydropyran (I; R=H or Me; R′=alkyl), itself the product of thermal addition of an alkyl vinyl ether to the acrolein (Longley and Emerson 1950; Smith, Norton, and Ballard 1951), namely,



(II)

In addition, substituted pentane-1,5-dialdehydes (type II) have been obtained by the reaction of an acrolein homologue with an alcohol in the presence of alkali (Bewley *et al.* 1954); but the dialdehyde is usually contaminated with the isomeric δ-lactone (Hall 1954). This procedure is an adaptation of the Michael

* For preliminary paper, see Cavill, G. W. K. *et al.* (1958).—*Chem. & Ind.* **1958**: 292.

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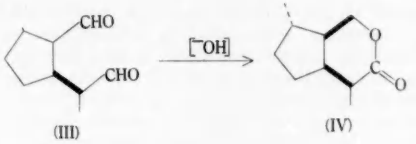
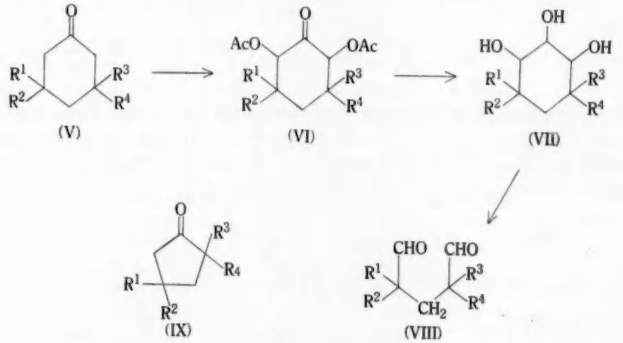
addition (Meerwein 1920), in which *iso*butyraldehyde was condensed with 2-methyl-3-ethylacrolein to yield 2,2,4-trimethyl-3-ethylpentane-1,5-dialdehyde, which in the presence of the alkaline catalyst, was isomerized to a δ-lactone. Conversion of the naturally occurring iridodial (III) into a mixture of lactones, including *iso*iridomyrmecin (IV) (Cavill, Ford, and Locksley 1956), is a more recent example of the 1,5-dialdehyde–δ-lactone rearrangement. As it is our intention to investigate the properties and reactions of 1,5-dialdehydes, including this rearrangement, a general synthetic approach is required which does not employ alkaline reaction conditions.



(III) (IV)

II. Synthesis of 1,5-Dialdehydes

Laboratory procedures for the synthesis of glutardial have been reinvestigated by Cope *et al.* (1951), who used the fission of *cyclo*hexane-1,2,3-triol (from phloroglucinol), and the Shaw synthesis (from pyridine). The present method is a generalization of the glycol fission procedure: the appropriately substituted alkyl*cyclo*hexanone (V) is oxidized with lead tetra-acetate in benzene solution (Cavill and Solomon 1955) to yield the 2,6-diacetoxy*cyclo*hexanone (VI), and



(V) (VI) (VII) (IX) (VIII)

this product is then reduced (lithium aluminium hydride) to the *cyclo*hexane-1,2,3-triol (VII) (cf. Prostenik and Bisean 1950), which is cleaved with sodium periodate to the required alkylpentane-1,5-dialdehyde (VIII). Alternatively, the action of lead tetra-acetate in acetic acid solution on a *cyclo*pentanone (type IX) yields the monoacetoxy derivative, which is reduced to the *cyclo*pentane-1,2-diol, and thence to the dialdehyde (VIII). As the *cyclo*hexanones (type V) are more readily synthesized than *cyclo*pentanones (type IX), the former procedure is the preferred one.

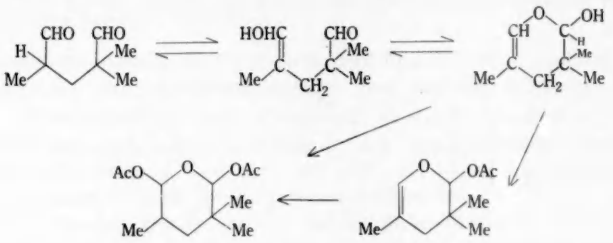
The *cyclo*hexanones (V; $R^1=R^2=R^3=R^4=H$ or Me) have been oxidized with lead tetra-acetate in benzene solution to yield a mixture of the 2-acetoxy- and 2,6-diacetoxy*cyclo*hexanones (see Table 1). Where the original ketone is unsymmetrical (V; $R^1=Me$, $R^2=R^3=R^4=H$; $R^1=R^2=R^3=Me$, $R^4=H$), the structure of the monoacetoxy derivative has been assigned on the basis that acetoxylation proceeds via the enol (Cavill and Solomon 1955), such enolization being determined by the Saytzeff rule. On further treatment with lead tetra-acetate in benzene solution, the monoacetoxy ketone yields the diacetoxy derivative.

The catalytic reduction and hydrolysis of *cis*-2,6-diacetoxy*cyclo*hexanone to *cis-cyclo*hexane-1,2,3-triol has been reported previously, and on glycol fission, glutardial is formed. Similarly, 2-methylpentane-1,5-dialdehyde is obtained from 3-methyl*cyclo*hexanone via 3-methyl-2,6-diacetoxy*cyclo*hexanone and 4-methyl*cyclo*hexane-1,2,3-triol. The di-, tri-, and tetramethyldiacetoxy*cyclo*hexanones could not be hydrogenated (Raney nickel catalyst), even at 100 °C/100 atm; but lithium aluminium hydride readily reduced each of these more highly substituted diacetoxyketones to yield a mixture of the required *cyclo*hexane-1,2,3-triol, and the *cyclo*hexane-1,2-diol. Similarly, 3-methyl-2,6-diacetoxy*cyclo*hexanone gave a mixture of the 4-methyl*cyclo*hexane-1,2,3-triol and 4-methyl*cyclo*hexane-1,2-diol (cf. catalytic hydrogenation); hence the 1,2-diol must result from reduction of the intermediate *cyclo*hexane-1,2-dione, formed by an elimination from the 2,6-diacetoxy*cyclo*hexanone.* The diol is easily separated from the triol by chromatography on alumina.

Whilst glutardial and 2-methylglutardial are formed by the fission of the triol with lead tetra-acetate in benzene solution, more highly substituted triols do not react completely under these conditions. In acetic acid solution, 4,4,6-trimethyl*cyclo*hexane-1,2,3-triol readily absorbed one molecular proportion of the oxidant, then reacted more slowly with the second. The infra-red spectrum of the product showed absorptions at 3400, 1757, 1725 (infl.), and 1670 cm^{-1}, indicative of the hydroxyl, acetate, and aldehyde groups, and of the carbon-carbon double bond, respectively. An acetyl estimation (10·8 per cent.) confirmed the presence of this ester. Finally, acid hydrolysis yielded 2,2,4-trimethylpentane-1,5-dialdehyde, isolated as the bis-2,4-dinitrophenylhydrazone. The glycol fission product is thus formulated as a mixture of the dialdehyde (aldehydo and lactol forms), and of the mono- and diacetyl derivatives, namely, 1,5-Dialdehydo–lactol tautomerism has been reported previously for homophthaldehyde (Potts and Robinson 1955), and for iridodial (Cavill, Ford, and Locksley 1956). Accordingly, sodium metaperiodate fission of the more highly substituted triols is preferred, and under these conditions, 4,4-dimethyl-, 4,6-dimethyl-, 4,4,6-trimethyl-, and 4,4,6,6-tetramethyl*cyclo*hexane-1,2,3-triol yielded 2,2-dimethyl-, 2,4-dimethyl-, 2,2,4-trimethyl-, and 2,2,4,4-tetramethylpentane-1,5-dialdehyde, respectively.

* The process of elimination and reduction to the *cyclo*hexane-1,2-diol, which is competing with normal reduction to the triol, will be considered in detail in a later paper on the synthesis of 1,6-dialdehydes.

Each of the dialdehydes distilled, under reduced pressure, as a clear colourless liquid, which immediately polymerized to a glassy mass. The monomer is regenerated on distillation (cf. iridodial). As 2,2,4,4-tetramethylpentane-1,5-dialdehyde also polymerizes, enolization is not essential to polymer formation and it is possible that polymerization follows the normal acid catalysed path (cf. acetaldehyde), but in this case a linear polymer would be expected. Each of the dialdehydes has been characterized as the bis-2,4-dinitrophenylhydrazone.



III. Experimental

Melting points are uncorrected. Light petroleum has b.p. 40–60 °C. Alumina refers to aluminium oxide, Peter Spence, grade H. Neutralized alumina is prepared by washing grade H alumina with methanol–acetic acid (9 : 1), triturating it with hot methanol until all washings are neutral, and drying (oven) at 150–200 °C. Organic solutions were dried over anhydrous magnesium sulphate, unless otherwise reported. Carbon, hydrogen, and nitrogen microanalyses are by Dr. E. Challen and Miss J. Johnston, and infra-red spectra by Mr. I. Reece, of this University.

(*a*) *Oxidation of* cyclo*Hexanones.*—Oxidation of 3-methyl-, 3,3-dimethyl-, 3,5-dimethyl-, 3,3,5-trimethyl-, and 3,3,5,5-tetramethyl*cyclo*hexanone with lead tetra-acetate in benzene solution, follows the procedure already reported (Cavill and Solomon 1955). Results are recorded in Table 1, for example :

(i) 3,3,5-Trimethyl*cyclo*hexanone (140 g ; Wicker 1956) with lead tetra-acetate (443 g) in benzene (2 l.) was heated under reflux until test (starch-iodide) for the oxidant was negative (7 hr). The benzene solution was then washed (water) and dried. Removal of the solvent, and then distillation under reduced pressure gave the unchanged ketone (20·0 g), b.p. 58–60 °C/6 mm and *6-acetoxy-3,3,5-trimethyl*cyclo*hexanone* (127 g) as a colourless oil, b.p. 116–117 °C/4·5 mm. Further distillation yielded *2,6-diacetoxy-3,3,5-trimethyl*cyclo*hexanone* (36 g) as an oil, b.p. 148–150 °C/2 mm, which slowly crystallized. The product was finally obtained as colourless prisms, m.p. 115–116 °C, from light petroleum.

(ii) 6-Acetoxy-3,3,5-trimethyl*cyclo*hexanone (120 g) treated with lead tetra-acetate (270 g) in benzene solution, as above, gave unchanged acetoxyketone (20 g), b.p. 97–101 °C/2 mm, and then 2,6-diacetoxy-3,3,5-trimethyl*cyclo*hexanone (110 g), finally isolated as colourless prisms, m.p. and mixed m.p. 115–116 °C, from light petroleum.

(*b*) *Reduction of 2,6-Diacetoxy*cyclo*hexanones.*—(i) Hydrogenation (Adams's catalyst) of 2,6-diacetoxy-3-methyl*cyclo*hexanone (5·0 g) in ethanol (200 ml) at 100 °C/100 atm, followed by acid hydrolysis (dilute HCl), gave *4-methyl*cyclo*hexane-1,2,3-triol* (2·4 g), 140–142 °C/3 mm, as a colourless liquid which partly solidified (cf. *cyclo*hexane-1,2,3-triol, Cavill and Solomon 1955).

(ii) The remaining triols were prepared by lithium aluminium hydride reduction of the diacetoxyketone, and the results are recorded in Table 2, for example, 2,6-diacetoxy-3-methyl-*cyclo*hexanone (15·0 g) was slowly added (30 min) to a suspension of lithium aluminium hydride (6·3 g) in ether (500 ml). When the exothermic reaction had subsided, the mixture was heated

TABLE 1

Substituted *cyclo*Hexanone	Monoacetate*	Boiling Point	Percentage Analysis				Diacetate*	Boiling Point	Percentage Analysis			
			Found		Calculated				Found		Calculated	
			C	H	C	H			C	H	C	H
3-Methyl- (112 g) (Knoevenagel 1897)	6-Acetoxy-3-methyl- (68 g)	96–100 °C/ 5 mm	63·8	8·1	63·5	8·3	2,6-Diacetoxy-3-methyl- (25 g)	129–131 °C/ 2 mm	58·1	7·0	57·9	7·1
3,3-Dimethyl- (50 g) (Henshall 1943)	6-Acetoxy-3,3-dimethyl- (46 g)	104–110 °C/ 2·5 mm	65·4	8·5	65·2	8·8	2,6-Diacetoxy-3,3-dimethyl- (10 g)	136–139 °C/ 2 mm	59·4	7·3	59·5	7·5
3,5-Dimethyl- (35 g) (Knoevenagel 1897)	2-Acetoxy-3,5-dimethyl- (35 g)	108–110 °C/ 3 mm	65·5	8·7	65·2	8·8	2,6-Diacetoxy-3,5-dimethyl- (7·7 g)	140–142 °C/ 3 mm (m.p. 119–120 °C)	59·2	7·4	59·5	7·5
3,3,5-Trimethyl- (140 g) (Wicker 1956)	6-Acetoxy-3,3,5-trimethyl- (127 g)	116–117 °C/ 4·5 mm	66·9	9·3	66·6	9·2	2,6-Diacetoxy-3,3,5-trimethyl- (36 g)	148–150 °C/ 2 mm (m.p. 115–116 °C)	61·0	7·8	60·9	7·9
3,3,5,5-Tetramethyl- (47 g) (Kharasch and Tawney 1941)	2-Acetoxy-3,3,5,5-tetramethyl- (37 g)	112–118 °C/ 3 mm (m.p. 40–41 °C)	68·1	9·5	67·9	9·5	2,6-Diacetoxy-3,3,5,5-tetramethyl- (5·7 g)	138–142 °C/ 1 mm	62·7	8·2	62·2	8·2

* Yields of monoacetate and diacetate reported are those from the same oxidation of the original ketone. The monoacetoxy ketone is further oxidized, in good yield, to the diacetoxy derivative.

TABLE 2

Substituted 2,6-Diacetoxy-*cyclo*hexanone	*cyclo*Hexane-1,2-diol*	*cyclo*Hexane-1,2,3-triol	Boiling Point	Percentage Analysis				Isolation Procedure
				Found		Calculated		
				C	H	C	H	
3-Methyl- (15·0 g)	4-Methyl- (1·0 g)	4-Methyl- (7·0 g)	168–170 °C/7 mm	57·5	9·8	57·5	9·7	Preferential ether extraction
3,3-Dimethyl- (30·0 g)	4,4-Dimethyl- (1·6 g)	4,4-Dimethyl- (14·0 g)	150–156 °C/6 mm	59·7	10·0	59·9	10·1	Chromatography
3,5-Dimethyl- (27·0 g)	3,5-Dimethyl- (1·8 g)	4,6-Dimethyl- (13·1 g)	(m.p. 155 °C)	60·2	9·8	59·9	10·1	Chromatography
3,3,5-Trimethyl- (10·2 g)	4,6,6-Trimethyl- (0·6 g)	4,4,6-Trimethyl- (5·7 g)	156–157 °C/4 mm	61·8	10·4	62·0	10·4	Chromatography
3,3,5,5-Tetramethyl- (23·4 g)	3,3,5,5-Tetramethyl- (1·5 g)	4,4,6,6-Tetramethyl- (12·1 g)	(m.p. 144–146 °C)	64·1	10·5	63·8	10·7	Chromatography

* Structure of each of the 1,2-diols was confirmed by oxidation to the dioic acid (or to the diol). (See footnote, p. 123.)

TABLE 3

*cyclo*Hexane-1,2,3-triol	Oxidant	Solvent	Pentane-1,5-dialdehyde	Boiling Point	Percentage Analysis				M.P. of Bis-2,4-dinitrophenylhydrazone (°C)	Percentage Analysis					
					Found		Calculated			Found			Calculated		
					C	H	C	H		C	H	N	C	H	N
Unsubstituted (13·2 g)	$Pb(OAc)_4$	Benzene	Unsubstituted (5·0 g)	60–62 °C/4 mm†					194–195‡			24·2			24·3
4-Methyl- (1·8 g)	,,	,,	2-Methyl-*						192–193§			23·7		•	23·6
4,4-Dimethyl- (10·0 g)	Sodium meta-periodate	Water	2,2-Dimethyl- (6·2 g)	72 °C/3 mm	65·9	9·7	65·6	9·4	228–230	46·8	4·2	22·8	46·7	4·5	22·9
4,6-Dimethyl- (10·0 g)	,,	,,	2,4-Dimethyl- (5·3 g)	97–100 °C/8 mm	65·8	9·4	65·6	9·4	218–222	46·9	4·3	22·7	46·7	4·5	22·9
4,4,6-Trimethyl- (5·8 g)	,,	,,	2,2,4-Trimethyl- (3·9 g)	96–100 °C/8 mm	67·5	10·0	67·6	9·9	270–272	47·7	4·3	22·3	47·8	4·4	22·3
4,4,6,6-Tetramethyl- (4·7 g)	,,	,,	2,2,4,4-Tetramethyl- (3·1 g)	103–105 °C/9 mm	69·1	10·3	69·2	10·3	275–278	48·7	4·6	21·2	48·8	4·7	21·7

* Isolated as the bis-2,4-dinitrophenylhydrazone (2·1 g).

† Longley and Emerson (1950) record b.p. 75–81 °C/15 mm.

‡ Cope *et al.* (1951) record m.p. 192·5–193·3 °C.

§ Smith, Norton, and Ballard (1951) record m.p. 198–198·5 °C.

under reflux (4 hr) (negative Fehling's test). Excess reductant was decomposed by the cautious addition of water and the mixture acidified (10% H_2SO_4). The ethereal layer was separated, and the aqueous solution further extracted with ether (2 × 20 ml). The combined ethereal solution was washed (sodium hydrogen carbonate solution) and dried. After removal of the solvent, 4-methyl*cyclo*hexane-1,2-diol (1·0 g) was obtained as a colourless oil, b.p. 118–120 °C/4 mm. The combined aqueous layers (including the wash solutions) were then neutralized (sodium hydrogen carbonate) and continuously extracted with ether (48 hr). This ether solution yielded 4-methyl*cyclo*hexane-1,2,3-triol (7·0 g), b.p. 168–170 °C/7 mm, as a semi-solid mass [cf. (i) above].

Alternatively, the diol and triol were separated as follows: 2,6-diacetoxy-3,3,5-trimethyl-*cyclo*hexanone (10·2 g) with lithium aluminium hydride (4·0 g) in ether (200 ml), treated as above, gave a viscous oil (6·5 g), b.p. 140–143 °C/2 mm. Then purification by chromatography on neutralized alumina yielded *4,6,6-trimethyl*cyclo*hexane-1,2-diol* (0·6 g), eluted with benzene. Further elution with ethanol gave *4,4,6-trimethyl*cyclo*hexane-1,2,3-triol* (5·7 g), b.p. 156–157 °C/4 mm, which partly crystallized on standing.

(*c*) *Fission of* cyclo*Hexane-1,2,3-triols.*—Results are reported in Table 3, for example: (i) 4,4-dimethyl*cyclo*hexane-1,2,3-triol (10·0 g) was suspended in water (500 ml), sodium metaperiodate (27 g) was added and the mixture stirred (1 hr). The product was extracted with ether (4 × 50 ml), and the ethereal layer dried. Evaporation of the solvent, then distillation under reduced pressure, gave *2,2-dimethylpentane-1,5-dialdehyde* (6·2 g), b.p. 72 °C/3 mm, as a colourless liquid, which rapidly polymerized on standing.

The *bis-2,4-dinitrophenylhydrazone*, prepared in the usual manner, was isolated as orange-red needles, m.p. 228–230 °C, from dimethylformamide.

(ii) 4,4,6-Trimethyl*cyclo*hexane-1,2,3-triol (14·8 g) in acetic acid (250 ml) was treated with lead tetra-acetate (75 g). The first molecular proportion of the oxidant reacted exothermally, but the second reacted only on standing overnight. Water (200 ml) was then added and the mixture extracted with chloroform (6 × 20 ml). The chloroform layer was washed ($NaHCO_3$ solution) and dried. Removal of the solvent, then distillation under reduced pressure, gave a pleasant smelling *product* (9·6 g), b.p. 94-100 °C/8 mm (Found: C, 61·4; H, 8·8; Ac, 10·8%. Calc. for $C_8H_{14}O_2$: C, 67·6; H, 9·9; Ac, 0·0%). The product, after solution in ethanol containing a trace of hydrochloric acid, readily yielded *2,2,4-trimethylpentane-1,5-dialdehyde bis-2,4-dinitrophenylhydrazone*, isolated as red needles, m.p. 270–272 °C, from dimethylformamide.

(iii) 4,4,6-Trimethyl*cyclo*hexane-1,2,3-triol (5·8 g), with sodium metaperiodate (14·4 g) in water (75 ml), treated as in (i), gave *2,2,4-trimethylpentane-1,5-dialdehyde* (3·9 g), b.p. 96–100 °C/8 mm. The bis-2,4-dinitrophenylhydrazone had m.p. and mixed m.p. 270–272 °C.

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COMPOUNDS DERIVED FROM β–SUBSTITUTED GLUTARIC ACIDS: GLUTARIMIDES, GLUTARAMIC ACIDS, 1,5–PENTANE DIOLS

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Summary

A series of β-substituted glutarimides have been prepared via the Guareschi synthesis of αα′-dicyano-ββ-dialkylglutarimides, the scope of which is discussed.

Two related series, ββ-dialkylglutaramic acids and 3,3-dialkylpentane diols, have been investigated. Representative αα′-dicarboxyamidoglutarimides and 1,1,3,3-tetracarboxylic acid propane di-imides, intermediates in the acid hydrolysis of the αα′-dicyanoglutarimides to glutarimides have been incidentally prepared.

Pharmacological findings for these series are briefly reported.

I. INTRODUCTION

The condensation of aliphatic ketones with cyanoacetic ester and ammonia has been well established as a general reaction for the preparation of αα′-dicyano-ββ-dialkylglutarimides (Guareschi 1901, 1919). Hydrolysis with aqueous sulphuric acid provides the ββ-dialkylglutaric acids in good yields (Guareschi 1901, 1919; Vogel 1934). A number of β-substituted glutarimides, prepared by reaction of the glutaric anhydride with ammonia or urea, have also been reported (Thole and Thorpe 1911), as well as several *N*-alkyl derivatives obtained by reacting the anhydride with a primary amine (Benica and Wilson 1950).

Until recently, little attention had been given to the pharmacology of glutarimides, but the discovery (Shaw *et al.* 1954) of the analeptic activity of β-ethyl β-methyl glutarimide (Bemegride, "Megimide"), and its subsequent success as a barbiturate antagonist (Shulman *et al.* 1955) led to our investigation of a large number of homologous β-substituted glutarimides and related compounds. The introduction in 1955 of αα-ethyl phenyl glutarimide (Glutethimide, "Doriden") (Tagmann, Sury, and Hoffmann 1952*a*, 1952*b*), a new type of sedative hypnotic, added further interest to compounds of this type.

In a preliminary paper (Somers 1956) the finding of both analeptic and hypnotic activity in other β-substituted glutarimides was reported. The present paper deals with the synthesis of these and further compounds in the series and also the preparation of related ββ-dialkylglutaramic acids, 2,2-dialkyl-1,1,3,3-tetracarboxylic acid propane di-imides, and 3,3-dialkyl-1,5-pentane diols.

II. DISCUSSION

The reactivity of ketones in the Guareschi synthesis of αα′-dicyano-ββ-disubstituted glutarimides (I) varies considerably with the nature of the substituent groups. Methyl *n*-alkyl ketones without exception may be condensed

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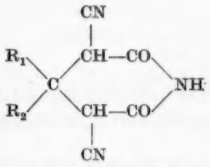
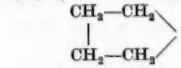
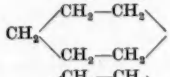
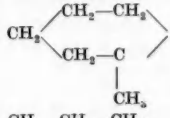
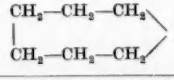
TABLE 1

αα′-DICYANO-β-SUBSTITUTED GLUTARIMIDES



Substituent Groups		Melting Point (°C) Found	Yield (%)	Melting Point (°C) Reported
R_1	R_2			
CH_3	CH_3	214–215	69	216–217 (Guareschi & Grande 1899)
CH_3	C_2H_5	192–193	73	193 (Guareschi 1898)
CH_3	CH_2CHOH	—	0	—
CH_3	$CH_2COOC_2H_5$	—	0	—
CH_3	*n*-C_3H_7	202–203	79	201–202 (Minozzi 1900)
CH_3	*iso*-C_3H_7	234–236	13	234–236 (Kon & Thorpe 1919)
CH_3	*n*-C_4H_9	174–175	77	180–182 } (Guareschi 1901)
CH_3	*iso*-C_4H_9	237–238	39	241 } (Guareschi 1901)
CH_3	*n*-C_5H_{11}	166–167	65*	—
CH_3	*iso*-C_5H_{11}	196–197	62†	—
CH_3	*n*-C_6H_{13}	152–153	50	154–155 (Guareschi & Grande 1899)
CH_3	*iso*-C_6H_{13}	161–166	64	166·5–168·5 (Guareschi 1901)
CH_3	*n*-C_7H_{15}	147·5–149	58‡	—
CH_3	*n*-C_9H_{19}	136	80	136·5–137·5 (Guareschi 1901)
CH_3	$(C_2H_5)_2NCH_2CH_2$	—	0	—
CH_3	C_6H_5	275 (decomp.)	2	270 (decomp.) (Guareschi 1901)
CH_3	$C_6H_5CH_2$	249–250	76	249–250 (Kon & Thorpe 1919)
C_2H_5	C_2H_5	204–206	35	200 (Peano 1901)
C_2H_5	*n*-C_5H_{11}	—	0	—
C_2H_5	C_6H_5	—	0	—
n-C_3H_7	*n*-C_3H_7	215–216	9	220–225 (Guareschi 1901)
iso-C_4H_9	*iso*-C_4H_9	—	0	—
C_6H_5	C_6H_5	—	0	—
		179–180	17	179–180 (Guareschi & Grande 1899)
		208–210	74	211–212 (Guareschi 1911)
		243 (decomp.)	16	245 (decomp.) (Kon & Thorpe 1919)
		205–206	8	203·5–204 (Nelson *et al.* 1920)

* Calc. for $C_{12}H_{17}O_2N_3$: C, 63·1; H, 6·9; N, 17·1%. Found: C, 63·3; H, 6·9; N, 17·4%.

† Calc. for $C_{13}H_{17}O_2N_3$: C, 63·1; H, 6·9; N, 17·1%. Found: C, 63·4; H, 6·9; N, 16·5%.

‡ Calc for $C_{15}H_{21}O_2N_3$: C, 65·4; H, 7·7; N, 15·3%. Found: C, 65·4; H, 7·7; N, 15·4%.

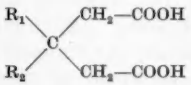
with ethyl cyanoacetate and ammonia to give the dicyanoimides in reasonably good yields (Table 1). However, branching of the alkyl substituent generally results in decreased yields. The reactivity of the ketone increases as the *iso*alkyl series is ascended, so that it seems evident that steric factors apply here. Similarly, whereas acetophenone could be condensed to give only a 2 per cent. yield of dicyanoglutarimide, and neither propiophenone nor benzophenone react at all, methyl benzyl ketone is highly reactive. Of the ethyl *n*-alkyl ketones tried in addition to methyl ethyl ketone, only diethyl ketone could be reacted (35 per cent. yield) and Vogel (1934) reported a 17 per cent. yield for the reaction with ethyl *n*-propyl ketone—no reaction was observed with ethyl *n*-amyl ketone. Where both alkyl groups are larger than methyl, the limit of reactivity in the series appears to be reached with di-*n*-propyl ketone which is very weakly reactive. Of the four cyclic ketones tested, only *cyclo*hexanone is as reactive as the methyl *n*-alkyl ketones, the yield obtained being 74 per cent., whereas 2-methyl*cyclo*hexanone gave only 16 per cent. yield of dicyanoimide. The main product from each of two *cyclo*pentanone reactions was ethyl *cyclo*pentylidene cyanoacetate (53 per cent.), the result of 1 : 1 Knoevenagel condensation, catalysed by ammonia. Vogel (1934) reported a 55 per cent. yield of the normal condensation product from the reaction.

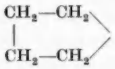
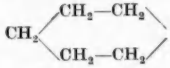
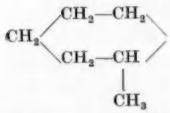
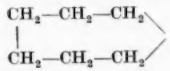
Recent investigations by McElvain and Clemens (1958) have shown that such ketones as acetophenone and propiophenone which yield little or no product in the normal Guareschi condensation can be made to give the dicyanoglutarimides in good yields by use of a two-stage condensation in which cyanoacetamide is condensed with the Knoevenagel condensation product in the presence of sodium ethoxide. Although we found this same procedure with ammonia as catalyst to result in marked improvement in yield of αα′-dicyano-ββ-methyl phenyl glutarimide (27 per cent. by two-stage reaction compared with 2 per cent. by Guareschi condensation) it was quite unsuccessful with propiophenone and benzophenone which are completely unreactive in the Guareschi condensation. In such cases, the use of more strongly alkaline conditions apparently forces the reaction. Their finding makes many other ββ-disubstituted glutaric acid derivatives accessible by synthesis.

Hydrolysis with 60 per cent. w/w sulphuric acid invariably results in high yields from ββ-dialkyl and β-*spirocyclo*alkane αα′-dicyanoglutarimides (Table 2). However, as noted by Kon and Stevenson (1921), similar treatment of the β-benzyl β-methyl compound does not lead to the glutaric acid, as decomposition occurs. The hydrolysis of the homologous β-methyl β-phenylimide also does not proceed smoothly under such hydrolysis conditions, but high yields of the glutaric acid are obtained by use of 50–55 per cent. w/w sulphuric acid, although the reaction time required is about trebled (to 24 hr). Hydrolysis of β-*n*-amyl β-methyl, β-*n*-hexyl β-methyl, β-*iso*hexyl β-methyl, and β-methyl β-*n*-nonyl αα′-dicyanoglutarimides resulted in mixtures of the glutaric acid (IV) and the glutarimide (VII) in the proportions 4 : 1, 2 : 1, 2 : 1, and 1 : 1 respectively, the combined yields in each case being 70–90 per cent. Complete conversion to the glutarimide was found to occur in the hydrolysis of αα′-dicyano-β-*n*-heptyl β-methylglutarimide. Birch and Robinson (1942) recorded a similar finding

TABLE 2

β-SUBSTITUTED GLUTARIC ACIDS



Substituent Groups		Melting Point (°C) Found	Yield (%)	Melting Point (°C) Reported
R_1	R_2			
CH_3	H	84–85	71	85–86 (Howles, Udall, & Thorpe 1900)
C_2H_5	H	67–69	74	73 } (Day & Thorpe 1920)
n-C_3H_7	H	48–50	70	52 } (Day & Thorpe 1920)
iso-C_4H_9	H	47–48	50	48 (Knoevenagel 1898)
n-C_6H_{13}	H	36–38	62	37–38 (Curtis, Day, & Timmins 1923)
C_6H_5	H	154–155	65	154–155 (Michael 1887)
CH_3	CH_3	102–103	72	103–104 } (Guareschi 1901)
CH_3	C_2H_5	86–87	89	87 } (Guareschi 1901)
CH_3	*n*-C_3H_7	89–91	86	92 } (Guareschi 1901)
CH_3	*iso*-C_3H_7	100	90	100 (Kon & Thorpe 1919)
CH_3	*n*-C_4H_9	63–65	85	64–65 (Guareschi 1901)
CH_3	*iso*-C_4H_9	66–68	74	63–65 (Guareschi 1919)
CH_3	*n*-C_5H_{11}	73–74	91 (*a*)	—
CH_3	*iso*-C_5H_{11}	70–73	91 (*b*)	—
CH_3	*n*-C_6H_{13}	66–67	76 (*c*)	52–53 (Guareschi 1919)
CH_3	*iso*-C_6H_{13}	79–80	92 (*d*)	80–81 (Rakskit, Bhattacharyga, & Bardhan 1956)
CH_3	*n*-C_9H_{19}	44–47	78 (*e*)	46·5–47·5 (Guareschi 1919)
CH_3	C_6H_5	140–142	82 (*f*)	132–133 (Phalnikar & Nargund 1937)
C_2H_5	C_2H_5	108	81	108 (Guareschi 1901)
n-C_3H_7	*n*-C_3H_7	117–118	70	112–113 (Guareschi 1901)
		177–178	80	176–177 (Kon & Thorpe 1919)
		182–183	93	181 (Thole & Thorpe 1911)
		143–145	82	148 (Kon & Thorpe 1919)
		155–156	62 (*g*)	156 (Day, Kon, & Stevenson 1920)

(*a*) Calc. for $C_{11}H_{20}O_4$: C, 61·1; H, 9·3%. Found: C, 61·6; H, 9·3%.

(*b*) Calc. for $C_{11}H_{20}O_4$: C, 61·1; H, 9·3%. Found: C, 61·3; H, 9·4%.

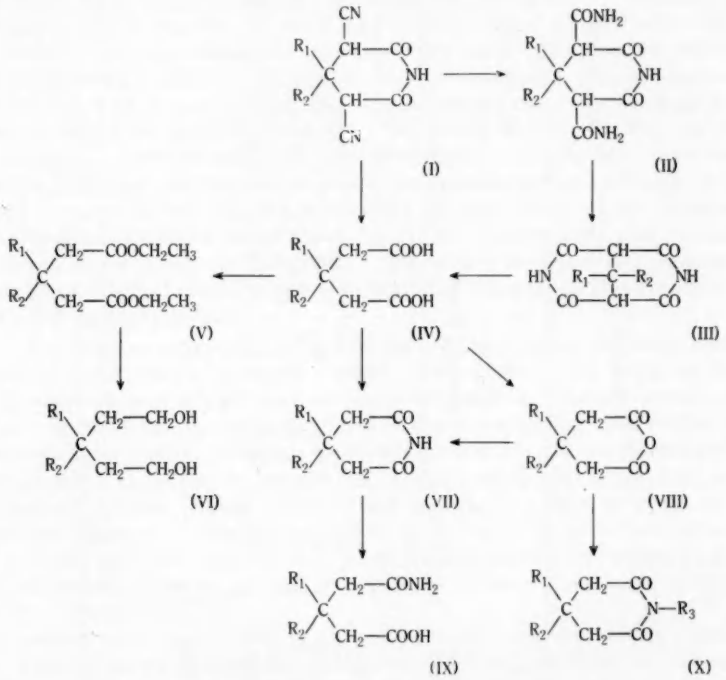
(*a*), (*c*), (*d*), (*e*) Yield includes acid and glutarimide. For CH_3, *n*-C_7H_{15} product was imide entirely—acid not prepared.

(*f*) Calc. for $C_{12}H_{14}O_4$: C, 64·9; H, 6·4%. Found: C, 64·7; H, 6·5%.

(*g*) Purified via the anhydride b.p. 180–190 °C/20 mm.

in the hydrolysis of αα′-dicyano-β-methyl β-*n*-octylglutarimide. In all other cases, the hydrolysis product was predominantly the glutaric acid, traces only of the glutarimide being detected.

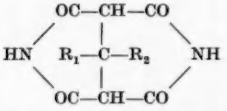
The acid hydrolysis apparently proceeds via the αα′-dicarboxyamido-glutarimides (II), but also involves the subsequent formation, by loss of ammonia, of the di-imide (III). Thorpe and Wood (1913) reported the preparation of the β-ethyl β-methyl, and β-*spirocyclo*hexane di-imides by solution of the αα′-dicyanoglutarimides in cold concentrated sulphuric acid. However, such



treatment resulted in our obtaining αα′-dicarboxyamido derivatives from the two lowest members of the β-methyl β-*n*-alkyl series, and mixtures of types II and III from the four higher homologues. The pure di-imides (Table 3) were obtained without difficulty by heating the αα′-dicyanoglutarimides briefly with 60 per cent. w/w sulphuric acid, by which means the two αα′-dicarboxyamido derivatives were also cyclized. No attempt was made to identify other hydrolysis intermediates. Several 2-alkyl 2-aryl di-imides of this type have also been reported by McElvain and Clemens (1958). αα′-Dicarboxyamido-β-ethyl β-methyl glutarimide is thermally degraded by heating above 300 °C to β-ethyl β-methyl glutarimide, although the yield was only 10 per cent. However, fairly

TABLE 3

2-SUBSTITUTED 1,1,3,3-TETRACARBOXYLIC ACID PROPANE DI-IMIDES



Substituent Groups		Melting Point (°C)	Yield (%)	Percentage Found			Formula	Percentage Calculated		
R_1	R_2			C	H	N		C	H	N
CH_3	CH_3	>360*	45							
CH_3	C_2H_5	329–331*	38	53·4	5·4	12·7	$C_{10}H_{12}O_4N_2$	53·6	5·4	12·5
CH_3	n-C_3H_7	278–280	85	55·6	5·8	11·8	$C_{11}H_{14}O_4N_2$	55·4	5·9	11·8
CH_3	n-C_4H_9	278–280	75	57·2	6·5	10·7	$C_{12}H_{16}O_4N_2$	57·1	6·4	11·1
CH_3	n-C_5H_{11}	237–238	70	59·1	7·0	10·4	$C_{13}H_{18}O_4N_2$	58·6	6·8	10·5
CH_3	n-C_6H_{13}	214	55	60·2	7·4	10·0	$C_{14}H_{20}O_4N_2$	60·0	7·2	10·0
CH_2—CH_2 / CH_2 / CH_2—CH_2		>370*	65							

* Reported by Thorpe and Wood (1913), m.p. as above.

smooth conversion in 60 per cent. yield is obtained by heating in aqueous medium for 2 hr at 220 °C and 70 atm carbon dioxide.

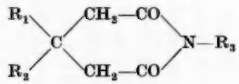
Glutarimides have previously been prepared by reaction of the glutaric anhydride (VIII) with urea or ammonium carbonate at 160–190 °C (Thole and Thorpe 1911) and by dry distillation of the ammonium glutarate salt (Sircar 1927). It was found that the glutarimides (VII) may be more conveniently obtained, in slightly improved yields directly from the glutaric acids by fusion with urea and heating at 170–190 °C. Reaction of the parent glutaric acid with urea at 160–170 °C gave a mixture of glutaric acid diamide and glutarimide, the latter being the only product from reaction above 180 °C. Succinic acid similarly gave a mixture of imide and diamide when reacted with urea at 160–170 °C. In each case, the products were easily separated by fractional recrystallization. Adipic acid diamide was the sole product from reaction of adipic acid with urea, and ring closure to adipimide could not be obtained by heating above its melting point—the imide is not recorded in the literature. In contrast, β-substituted glutaric acid diamides were not similarly obtained by reaction with urea at lower temperatures, the glutarimide being the only product in all cases (Table 4). In this connection, the preparation of the three lower ββ-methyl *n*-alkyl glutarimides by reaction of the glutaric acids with formamide has been reported recently (Abe 1957). The various *N*-substituted glutarimides were prepared by standard methods, involving reaction of the glutaric anhydride with the appropriate base.

The aqueous solubilities of the ββ-dialkyl glutarimides generally decrease sharply as the series is ascended, β-ethyl β-methyl glutarimide being soluble to the extent of only 0·5 per cent. at room temperature. Sodium salts, having about 10 times the aqueous solubilities of the corresponding free imides, were prepared from β-ethyl β-methyl, β-*iso*propyl β-methyl, and β-*spirocyclo*pentane glutarimide. However, hydrolysis rate determinations, involving titration of aliquots of solution against standard acid at increasing time intervals, showed that the amount of glutarimide present in the useful range of concentrations (2 to 5 per cent. salt solution) falls to about half the original values in 2–3 hr at room temperature, as a result of hydrolysis to the corresponding glutaramic acid.

Jeffery and Vogel (1934) prepared glutaramic acid by partial hydrolysis of diethyl glutarate followed by reaction with ammonia to form the half amide. Other glutaramic acids could presumably be similarly obtained. However, a more convenient method is that of hydrolysis of the corresponding glutarimide with an equivalent of sodium hydroxide, the glutaramic acid (IX) being obtained in almost quantitative yield and high purity. A series of such ββ-dialkyl glutaramic acids have been prepared in this way (Table 5). Succinamic acid may be similarly obtained from the imide. As with succinamic acid, ring closure to the imides is easily obtained by heating the glutaramic acids above their melting points. The glutaramic acids are more stable to hydrolysis than succinamic or phthalamic acids in that they may be recrystallized from water without noticeable change, but on prolonged boiling in aqueous solution the corresponding glutaric acid is obtained.

TABLE 4

β-SUBSTITUTED GLUTARIMIDES

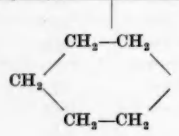
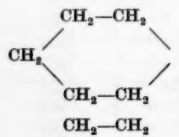
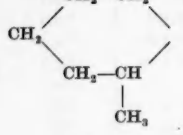
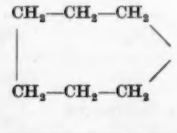


Substituent Groups			Melting Point (°C) or Boiling Point (°C/mm) Found	Yield (%)	Melting Point (°C) or Boiling Point (°C/mm) Reported	Percentage Found			Formula	Percentage Calculated		
R_1	R_2	R_3				C	H	N		C	H	N
H	H	H	151–152	74	152 (Sircar 1927)							
CH_3	H	H	142–143	58	142–143 (Sircar 1927)							
CH_3	H	$C_6H_5CH_2CH_2$	100–101	61	98–100 (Paden & Adkins 1936)							
C_2H_5	H	H	84–85	53	87 (Mallard & Wilson 1957)							
n-C_3H_7	H	H	113–113·5	70		62·1	8·5	9·2	$C_8H_{13}O_2N$	61·9	8·4	9·0
iso-C_3H_7	H	H	118–120	80	120 (Howles & Thorpe 1899)							
iso-C_4H_9	H	H	138–138·5	70		63·9	8·9	8·4	$C_9H_{15}O_2N$	63·9	8·9	8·3
n-C_6H_{13}	H	H	112–113	72	115 (Curtis, Day & Kimmins 1923)							
C_6H_5	H	H	173–174	75	173–174 (Mallard & Wilson 1957)							
C_6H_5	H	CH_3	141–142	62	141–142 (Mallard & Wilson 1957)							
C_6H_5	H	C_2H_5	94	79		71·7	6·9	6·6	$C_{12}H_{15}O_2N$	72·0	7·0	6·5
CH_3	CH_3	H	144	80	144 (Perkin & Thorpe 1899)							
CH_3	CH_3	CH_3	56–58	81	51–55 (Benica & Wilson 1950)							
CH_3	C_2H_5	H	126–127	71	125–126 (Thole & Thorpe 1911)							
CH_3	C_2H_5	CH_3	126–130/7[a]	61	115/7 (Benica & Wilson 1950)							
CH_3	C_2H_5	C_2H_5	110–112/6[b]	60	111/6 (Benica & Wilson 1950)							
CH_3	C_2H_5	C_6H_5	128	65		73·1	7·4	6·1	$C_{14}H_{17}O_2N$	72·7	7·4	6·1
CH_3	C_2H_5	*p*-$C_6H_4CH_3$	150–151	74		73·6	7·8	5·8	$C_{15}H_{19}O_2N$	73·4	7·8	5·7

TABLE 4 (*Continued*)

Substituent Groups			Melting Point (°C) or Boiling Point (°C/mm) Found	Yield (%)	Melting Point (°C) or Boiling Point (°C/mm) Reported	Percentage Found			Formula	Percentage Calculated		
R_1	R_2	R_3				C	H	N		C	H	N
CH_3	C_2H_5	$C_6H_5—CH_2$	160/1[c]	69		73·2	7·7	5·9	$C_{13}H_{19}O_2N$	73·4	7·8	5·7
CH_3	*n*-C_3H_7	H	119–120	46	117–118 (Benica & Wilson 1950)							
CH_3	*iso*-C_3H_7	H	165–166	90		64·1	9·0	8·4	$C_9H_{15}O_2N$	63·9	8·9	8·3
CH_3	*iso*-C_3H_7	CH_3	165–170/25[d]	75		64·9	9·4	7·8	$C_{10}H_{17}O_2N$	65·4	9·3	7·7
CH_3	*n*-C_4H_9	H	115–115·5	63		65·4	9·1	7·7	$C_{10}H_{17}O_2N$	65·5	9·3	7·7
CH_3	*n*-C_4H_9	CH_3	140/7[e]	67		66·5	9·6	7·1	$C_{11}H_{19}O_2N$	67·0	9·7	7·1
CH_3	*n*-C_4H_9	C_2H_5	136/6[f]	63		67·9	10·0	7·1	$C_{12}H_{21}O_2N$	68·3	10·0	6·6
CH_3	*iso*-C_4H_9	H	103–104	90		65·9	9·2	7·6	$C_{10}H_{17}O_2N$	65·5	9·3	7·7
CH_3	*n*-C_5H_{11}	H	113–114	74		67·4	9·7	7·2	$C_{11}H_{19}O_2N$	67·0	9·7	7·1
CH_3	*iso*-C_5H_{11}	H	120–121	78		67·3	9·6	7·0	$C_{11}H_{19}O_2N$	67·0	9·7	7·1
CH_3	*n*-C_5H_{11}	CH_3	132/4[g]	56		68·6	10·1	6·3	$C_{12}H_{21}O_2N$	68·3	10·0	6·6
CH_3	*n*-C_5H_{11}	C_2H_5	142/5[h]	61		69·3	10·0	6·6	$C_{13}H_{23}O_2N$	69·3	10·2	6·2
CH_3	*n*-C_6H_{13}	H	99·5–100·5	60		68·6	9·8	6·7	$C_{12}H_{21}O_2N$	68·3	10·0	6·6
CH_3	*n*-C_6H_{13}	CH_3	162/7[i]	49		69·1	10·4	6·9	$C_{13}H_{23}O_2N$	69·3	10·2	6·2
CH_3	*n*-C_6H_{13}	C_2H_5	160/6[j]	57		70·0	10·4	6·2	$C_{14}H_{25}O_2N$	70·3	10·5	5·9
CH_3	*iso*-C_6H_{13}	H	107–108·5	90		68·6	10·0	6·5	$C_{12}H_{21}O_2N$	68·3	10·0	6·6
CH_3	*n*-C_7H_{15}	H	95–96	90		69·5	10·1	6·4	$C_{13}H_{23}O_2N$	69·3	10·2	6·2
CH_3	*n*-C_9H_{19}	H	100	85		71·3	10·6	5·7	$C_{15}H_{27}O_2N$	71·1	10·7	5·5
CH_3	C_6H_5	H	156–157	90		71·4	6·5	6·9	$C_{12}H_{13}O_2N$	70·9	6·4	6·9
C_2H_5	C_2H_5	H	146–147	74	146–147 (Sircar 1927)							
n-C_3H_7	*n*-C_3H_7	H	125	71		67·4	9·8	7·1	$C_{11}H_{19}O_2N$	67·0	9·7	7·1
$CH_2—CH_2$		H	153	56	153 (Kon & Thorpe 1919)							
$CH_2—CH_2$												

TABLE 4 (*Continued*)

Substituent Groups			Melting Point (°C) or Boiling Point (°C/mm) Found	Yield (%)	Melting Point (°C) or Boiling Point (°C/mm) Reported	Percentage Found			Formula	Percentage Calculated		
R_1	R_2	R_3				C	H	N		C	H	N
		H	169–170	80	168 (Thole & Thorpe 1911)							
		CH_3	69–70	67	66 (Birch & Robinson 1942)							
		H	122–124	60		67·8	8·7	7·3	$C_{11}H_{17}O_2N$	67·7	8·8	7·2
		H	177–178	71	177–178·5 (Day, Kon, & Stevenson 1920)							

[a] n_D/22 °C, 1·4743. [b] n_D/22 °C, 1·4709. [c] n_D/22 °C, 1·5294. [d] n_D/22 °C, 1·4812. [e] n_D/20 °C, 1·4762. [f] n_D/20 °C, 1·4712. [g] m.p. 43–44 °C. [h] n_D/21 °C, 1·4708. [i] n_D/21 °C, 1·4745. [j] n_D/21 °C, 1·4717.

3,3-Dimethyl 1,5-pentane diol has been previously prepared by high pressure hydrogenation of the glutaric acid (Miller and Adams 1935). A series of 3,3-dialkyl 1,5-pentane diols (VI, Table 7) was obtained, in high yields, by lithium aluminium hydride reduction of the diethyl glutarates.

With regard to pharmacological screening of the compounds synthesized, the prime object was the discovery of analeptic and hypnotic compounds. No appreciable activity was found in the series of types I, II, III, IV, V, or IX. In the glutarimide series (Table 4), the hypnotic activities of β-*n*-butyl β-methyl, β-*n*-amyl β-methyl, and β-*n*-hexyl β-methyl glutarimides have been previously reported (Somers 1956). The *N*-methyl derivatives of these three imides are also hypnotic in mice, but the *N*-ethyl compounds had only very mild actions. Many of the other glutarimides listed were found to have convulsant effects in mice similar to that of β-ethyl β-methyl glutarimide (Bemegride, " Megimide "), the most active being β-methyl β-*iso*propyl glutarimide which is highly active as an analeptic and barbiturate antagonist. In the 1,5-pentane diol series (Table 7), sedative effects were prominent in all cases, the 3-*n*-butyl 3-methyl, 3-*n*-amyl 3-methyl, and 3-*n*-hexyl 3-methyl members having about equal hypnotic activities by intraperitoneal injection in mice to those of the corresponding glutarimides. The results of the pharmacological studies on these compounds will be reported more completely elsewhere.

III. Experimental

Microanalyses were carried out by the University of Melbourne and C.S.I.R.O. Microanalytical Laboratory. Melting points are uncorrected. The following general procedures were found satisfactory for preparation of all the compounds listed, with the few modifications mentioned in the text.

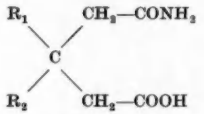
(*a*) *αα′-Dicyano-ββ-disubstituted Glutarimides.*—Alcohol (99·5%; 500 ml) was saturated with anhydrous ammonia at 0–5 °C over 1½–2 hr, and a mixture of ethyl cyanoacetate (2 moles; 226 g) and the ketone (1 mole) added. The solution was kept in a sealed flask at 0–5 °C for 1–5 days, when the precipitate was filtered and washed with ethanol. After solution in warm water (1200–1500 ml), addition of conc. HCl precipitated the imide which, after filtration, washing with water, and oven-drying, was sufficiently pure for conversion to the glutaric acid. The compounds crystallized from ethanol as colourless plates or needles.

In those cases where the final yield of product was low, or where no condensation occurred, the reaction precipitate was partly or wholly cyanoacetamide. The latter was separated by dissolving the mixture in warm water and precipitating the insoluble imide by the addition of conc. HCl. A further quantity of product was then obtained by dilution of the original alcoholic liquors with water (2 vols) and, after extracting several times with ether, acidifying the aqueous fraction to precipitate the imide. This was necessary only when the reaction yield was lower than 50%.

(*b*) *ββ-Dialkylglutaric Acids.*—The αα′-dicyano-ββ-dialkylglutarimide (0·5 mole) was dissolved with warming in conc. H_2SO_4 (250 ml) and water (250 ml) added slowly with shaking. The mixture was refluxed until no solid matter remained, an oily layer invariably separating at this stage. The mixture was transferred to a beaker and allowed to cool, when the crude hydrolysis product separated as a hard cake above the $(NH_4)_2SO_4$-H_2SO_4 liquors. The glutaric acid was purified by separating the cake, dissolving it in ether, washing the extract once with a small volume of water, then thoroughly extracting the ethereal solution with saturated $NaHCO_3$ solution. The extract was then acidified and finally extracted with ether. Evaporation of the solvent gave a colourless oil which readily crystallized. The acids may be recrystallized from light petroleum–benzene mixtures.

TABLE 5

ββ-DIALKYLGLUTARAMIC ACIDS



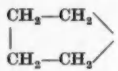
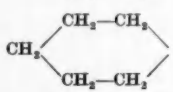
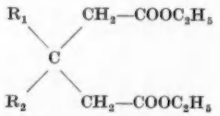
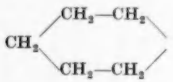
Substituent Groups		Melting Point (°C)	Yield (%)	Percentage Found			Equiv. Wt. Found	Formula	Percentage Calculated			Equiv. Wt. Calculated
R_1	R_2			C	H	N			C	H	N	
CH_3	C_2H_5	84–85	85	55·9	8·7	8·2	175	$C_8H_{15}O_3N$	55·5	8·7	8·1	173
CH_3	*n*-C_3H_7	98–99	88	58·1	9·1	7·6	184	$C_9H_{17}O_3N$	57·8	9·1	7·5	187
CH_3	*iso*-C_3H_7	118	85	57·8	9·1	7·4	192	$C_9H_{17}O_3N$	57·8	9·1	7·5	187
CH_3	*n*-C_4H_9	88–91	93	59·8	9·6	7·0	198	$C_{10}H_{19}O_3N$	59·7	9·5	7·0	201
CH_3	*iso*-C_4H_9	96	90	59·9	9·3	7·0	196	$C_{10}H_{19}O_3N$	59·7	9·5	7·0	201
CH_3	*n*-C_5H_{11}	86–88	95	61·4	10·0	6·6	211	$C_{11}H_{21}O_3N$	61·4	9·8	6·5	215
CH_3	*n*-C_6H_{13}	63–65	82	63·3	10·3	6·1	231	$C_{12}H_{23}O_3N$	62·9	10·1	6·1	229
C_2H_5	C_2H_5	130	90	58·1	9·2	7·5	183	$C_9H_{17}O_3N$	57·8	9·1	7·5	187
		110	85	58·8	8·0	7·5	185	$C_9H_{15}O_3N$	58·4	8·2	7·6	185
		141–145	80	60·9	8·7	6·8	205	$C_{10}H_{17}O_3N$	60·3	8·6	7·0	199

TABLE 6

DIETHYL ββ-DIALKYL GLUTARATES

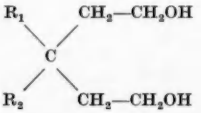


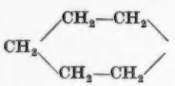
Substituent Groups		Boiling Point (°C/mm)	n_D/°C	Yield (%)	Percentage Found		Formula	Percentage Calculated	
R_1	R_2				C	H		C	H
CH_3	CH_3	93/2*	1·4290/21	67					
CH_3	C_2H_5	110/3	1·4343/21	76	63·0	9·8	$C_{12}H_{22}O_4$	62·6	9·6
CH_3	n-C_3H_7	114–115/3·5	1·4359/21	70	64·1	9·8	$C_{13}H_{24}O_4$	63·9	9·9
CH_3	n-C_4H_9	168/13	1·4339/28	60	65·0	10·1	$C_{14}H_{26}O_4$	65·1	10·1
CH_3	n-C_5H_{11}	170/14	1·4392/21	70	66·1	10·2	$C_{15}H_{28}O_4$	66·1	10·4
CH_3	n-C_6H_{13}	164/4	1·4414/21	73	67·2	10·4	$C_{16}H_{30}O_4$	67·1	10·6
		138–140/3·5	1·4573/25	78	66·0	9·4	$C_{14}H_{24}O_4$	65·6	9·4

* Perkin and Goodwin (1896) report b.p. 127–128 °C/15 mm.

TABLE 7

3,3-DIALKYL 1,5-PENTANE DIOLS



Substituent Groups		Boiling Point (°C/mm)	n_D/°C	Yield (%)	Percentage Found		Formula	Percentage Calculated	
R_1	R_2				C	H		C	H
CH_3	CH_3	131/3*	1·4510/26	50	63·3	12·0	$C_7H_{16}O_2$	63·6	12·2
CH_3	C_2H_5	160–162/10	1·4640/23	85	65·8	12·4	$C_8H_{18}O_2$	65·7	12·4
CH_3	n-C_3H_7	144/3	1·4618/26	75	67·6	12·3	$C_9H_{20}O_2$	67·5	12·6
CH_3	n-C_4H_9	134/0·5	1·4629/26	83	68·4	12·8	$C_{10}H_{20}O_2$	68·9	12·7
CH_3	n-C_5H_{11}	168–169/1	1·4640/23	80	70·4	13·0	$C_{11}H_{24}O_2$	70·2	12·9
CH_3	n-C_6H_{13}	182–184/1	1·4631/25	92	71·3	12·9	$C_{12}H_{26}O_2$	71·2	13·0
		166/2	1·4930/25	62	70·0	11·9	$C_{10}H_{20}O_2$	69·7	11·7

* Miller and Adams (1935) report b.p. 132 °C/1 mm.

The acid hydrolysis liquors contained a negligible amount of product and were not extracted. In the preparations where the hydrolysis product consisted of a mixture of the glutaric acid and the ββ-methyl *n*-alkyl glutarimide, the latter was obtained by evaporation of the dried ethereal solution remaining after extraction with aqueous $NaHCO_3$.

The five β-alkylglutaric acids were prepared by the method of Day and Thorpe (1920), involving condensation of the appropriate aldehyde with cyanoacetamide, using piperidine as catalyst, and subsequent hydrolysis of the αα′-dicyano-β-alkylglutaramide as for the dicyanoimides. β-Phenylglutaric acid was prepared from ethyl cinnamate by a Michael reaction with malonic ester.

Glutaric anhydrides were obtained by refluxing the acid with excess acetic anhydride for several hours, followed by concentration and finally distillation under reduced pressure.

The diethyl glutarates were obtained by refluxing the acid (0·2 mole) in absolute alcohol (200 ml) containing conc. H_2SO_4 (1 ml) for 8 hr. After cooling and dilution with water (400 ml), the solution was made alkaline with Na_2CO_3 and extracted thoroughly with ether. The ether extract was dried, evaporated, and the residue distilled under a vacuum, giving a colourless liquid.

(*c*) β-*Substituted Glutarimides.*—An intimate mixture of the glutaric acid (0·5 mole) and urea (1 mole ; 62 g) was heated in an oil-bath at 170–190 °C for 2–3 hr, when evolution of gases had ceased. The mixture solidified on cooling, and the product, after maceration with water and filtration, was recrystallized from water or ethanol. The compounds mostly crystallized as colourless plates, with low aqueous solubilities.

(*d*) β-*Substituted N-Substituted Glutarimides.*—The glutaric anhydride (0·1 mole) reacted exothermally with the appropriate primary amine (0·1 mole). Reaction was completed by heating the mixture in an oil-bath at 170–190 °C for 2–3 hr. In some cases the residue crystallized on cooling, when the product was purified by recrystallization from alcohol. Otherwise, the product was obtained by fractional distillation under reduced pressure. For the preparation of *N*-methyl and *N*-ethyl imides, an aqueous solution of the amine (0·11M) was added with mechanical stirring to the glutaric anhydride (0·1M) cooled in an ice-bath. The water was then boiled off and the residue heated in an oil-bath at 170–190 °C for 1–1½ hr, the product being distilled in a vacuum. These compounds are all colourless liquids or solids and are practically insoluble in water.

(*e*) ββ-*Dialkylglutaramic Acids.*—The glutarimide (0·1 mole) was added to a solution of NaOH (0·1 mole ; 4·0 g) in water (35 ml) and the solution refluxed for 30 min. After cooling and filtration through sintered glass, acidification with conc. HCl precipitated an oil which solidified on rubbing. Recrystallization from water gave a product of high purity. The acids crystallized as colourless needles, the lower members of the series being moderately soluble in water, the higher members almost insoluble. The glutarimides are smoothly regenerated from the glutaramic acids by heating for a few minutes at 160–180 °C.

(*f*) αα′-*Dicarboxyamido-ββ-dialkylglutarimides.*—The αα′-dicyano-ββ-dialkylglutarimide (5 g) was dissolved in conc. H_2SO_4 (20 ml) and the solution, after being allowed to stand for 24 hr, poured into ice water (40 ml). The precipitate which formed was collected and recrystallized from water. For the ββ-dimethyl derivative, colourless prisms, m.p. >330 °C in 70% yield (Found : C, 47·8 ; H, 5·8 ; N, 18·0%. Calc. for $C_9H_{13}O_4N_3$: C, 47·6 ; H, 5·8 ; N, 18·5%). For the ββ-methyl ethyl derivative, colourless prisms, m.p. 277 °C (decomp.) in 75% yield (Found : C, 50·2 ; H, 6·0 ; N, 17·5%. Calc. for $C_{10}H_{15}O_4N_3$: C, 49·8 ; H, 6·3 ; N, 17·4%).

(*g*) *2,2-Dialkyl-1,1,3,3-tetracarboxylic Acid Propane Di-imides.*—The αα′-diycano-ββ-dialkyl glutarimide (5 g) was dissolved in 60% aqueous H_2SO_4 (20 ml). After heating for a few minutes, the solution began to bubble and a white solid separated. The mixture was heated for 1 min further and then allowed to cool, when the precipitate was filtered, washed with water, and recrystallized from water. The compounds are colourless prisms, quite insoluble in cold water. Similar treatment of the αα′-dicarboxyamidoimides (Section III (*f*)) resulted in conversion to the corresponding di-imides.

(*h*) *3,3-Dialkyl 1,5-Pentane Diols.*—A solution of the diethyl glutarate (0·1 mole) in dry ether (50 ml) was added, over 10 min with mixing, to a slurry of finely powdered $LiAlH_4$ (0·125

mole) in dry ether (200 ml), after which the mixture was refluxed for ½ hr. After cooling, the complex was decomposed by addition of sufficient moist ether and finally H_2SO_4 (10%; 50 ml). The precipitate was filtered, washed with ether, and the combined ethereal solutions dried, evaporated, and the residue distilled under vacuum. The diols are colourless viscous liquids slightly soluble in water.

IV. Acknowledgments

We are grateful to Mrs. G. Galvin for valuable technical assistance during a part of these investigations, and to Mr. R. G. Curtis for helpful discussion.

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COORDINATION COMPOUNDS OF SUBSTITUTED 1,10-PHENANTHROLINES AND RELATED DIPYRIDYLS

I. SYNTHESIS OF 2,9-DIMETHYL-1,10-PHENANTHROLINE

By E. J. O'REILLY* and R. A. PLOWMAN*

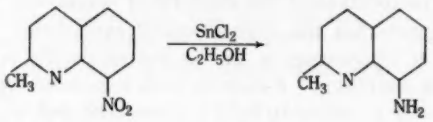
[*Manuscript received September* 8, 1959]

Summary

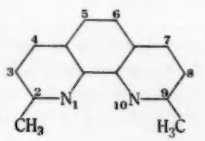
A direct synthesis of 2,9-dimethyl-1,10-phenanthroline has been developed. The method involves a Skraup type of reaction between *o*-phenylenediamine, crotonaldehyde, and either arsenic(V) oxide or sodium *m*-nitrobenzenesulphonate. Some derivatives of 2,9-dimethyl-1,10-phenanthroline have been characterized.

I. INTRODUCTION

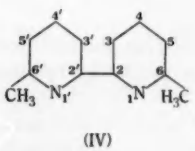
During an investigation into the syntheses of mono-, di-, and tetra-alkylated 1,10-phenanthrolines, Case (1948) successfully synthesized 2,9-dimethyl-1,10-phenanthroline (III). A Skraup reaction between *o*-nitroaniline and crotonaldehyde diacetate, using arsenic(V) oxide as the oxidizing agent, yielded 8-nitroquinaldine (I). Reduction of I with stannous chloride in ethanol solution gave 8-aminoquinaldine (II). From II, by further Skraup reaction with crotonaldehyde diacetate in presence of arsenic(V) oxide, 2,9-dimethyl-1,10-phenanthroline(III) was obtained. The recorded yield was about 7 per cent. based on I.



(I) (II)



(III)



(IV)

This synthesis has been modified (Geigy 1952) by subjecting II to a Skraup reaction with crotonaldehyde in the presence of 65 per cent. sulphuric acid as solvent and condensing agent, and oxidizing with *m*-nitrobenzenesulphonic acid. After reaction, the mixture was diluted, neutralized, and the precipitated " tar " extracted with benzene, from which III was obtained in yields of 60–70 per cent. based on II.

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II. Stereochemical Considerations

2,9-Dimethyl-1,10-phenanthroline is considered interesting from a stereochemical viewpoint. It has been well established that 1,10-phenanthroline readily coordinates to metal ions (Brandt, Dwyer, and Gyarfas 1954), for example, iron(II) salts yield a tris-substituted complex which is intensely coloured. However, 2,9-dimethyl-1,10-phenanthroline and also the analogous 6,6′-dimethyl-2,2′-dipyridyl (IV) produce no coloration with iron(II) salts under similar conditions (Burstall 1938; Case 1948; Hoste 1950; Irving, Cabell, and Mellor 1953).

It has been established that for a given metal there is a relationship between proton binding capacity of a ligand and the stability of the complex formed with the metal (Bjerrum 1950; Martell and Calvin 1952). Methyl substituents in the 2,9-positions of 1,10-phenanthroline should increase the base strength and hence should lead to an increase in stabilities of metal complexes formed. However, it has been proposed that methyl groups in the 2,9-positions cause effects which are not consistent with an explanation due to base strength but which require a stereochemical explanation (Brandt, Dwyer, and Gyarfas 1954). The formation of coloured complexes between iron(II) salts and the 1,10-phenanthrolines or the 2,2′-dipyridyls are due to the formation of 3 : 1 complexes, that is, complexes of the type $[ML_3]^{n+}$ where M=Fe and L is a bidentate ligand such as 1,10-phenanthroline or 2,2′-dipyridyl. Steric hindrance due to substitution in the 6,6′-positions of dipyridyl or 2,9-positions of phenanthroline manifests itself in interference between ligands and prevents them from forming favourably orientated bonds for octahedral tris-substituted complexes.

It is to be noted that the stereochemical explanation applies principally to the formation of tris-complexes, and is not so readily applicable to mono- and bis-substituted complexes. Failure to form a coloured complex with iron(II) salts is indicative only of failure to form a tris-substituted complex which failure is explained on the stereochemical consideration given above. The possibility exists that these substituted dipyridyl and phenanthroline molecules can form mono- and bis-substituted complexes of high stability and strong bonding to metal ions.

2,9-Dimethyl-1,10-phenanthroline has been used as a specific reagent for copper(I) and in particular for the spectrophotometric estimation of copper in the presence of iron. Use is made of an intensely orange-red coloured complex formed between copper(I) compounds and the base. Smith and McCurdy (1952) have determined spectrophotometrically, the molecular ratio of 2,9-dimethyl-1,10-phenanthroline to copper(I) in the orange coloured complex by the method of continuous variations and have found it to be 2 : 1 in both aqueous and alcoholic solutions. On this basis they have suggested the formula $[Cu(dimephen)_2]^+$ for the orange coloured compound.

Hoste (1950) has shown that in alcoholic solutions copper(I) coordinates 2 moles of 1,10-phenanthroline or 2,2′-dipyridyl. This was indicated by the fact that the concentration of copper being kept constant, the value of the extinction coefficient of the solution ceased to increase when the proportion of either reagent to copper attained the ratio of 2 : 1. Thus, in its reaction

with copper(I), 2,9-dimethyl-1,10-phenanthroline appears to be analogous to 1,10-phenanthroline or 2,2′-dipyridyl. However, these copper(I) compounds have not been isolated and characterized. In a patent granted to Geigy (1952), mention has been made of metal complexes of 2,9-dimethyl-1,10-phenanthroline being fungistatic when applied to textiles. The complexed metals were Cu, Zn, Hg, Ag, Cd, Fe, Co, and Ni.

To further characterize these and chelate compounds with other metals, we have investigated a new approach to the synthesis of 2,9-dimethyl-1,10-phenanthroline.

III. Results

1,10-Phenanthroline has been prepared directly by Skraup synthesis from *o*-phenylenediamine and glycerol in 65–70 per cent. sulphuric acid, arsenic(V) oxide being used as oxidizing agent (Halcrow and Kermac 1946). Quinaldine has been synthesized from aniline and crotonaldehyde or paraldehyde using either Skraup or Doebner-von Miller reactions (Manske 1942). It appeared that an analogous direct synthesis of 2,9-dimethyl-1,10-phenanthroline using *o*-phenylenediamine as starting material should be feasible. This has proved successful; *o*-phenylenediamine reacted with either crotonaldehyde or crotonaldehyde diacetate in 65–70 per cent. sulphuric acid if arsenic(V) oxide or *m*-nitrobenzenesulphonic acid was present as oxidizing agent. The primary product was a " tar " obtained by neutralizing the reaction mixture. 2,9-Dimethyl-1,10-phenanthroline was not readily extracted from this " tar " by the analogous methods used for the extraction of 1,10-phenanthroline or quinaldine, namely, benzene extraction or steam distillation. The only satisfactory method for isolation appeared to be the precipitation of a copper(II) chloride derivative from dilute hydrochloric acid or ethanol solution, which after isolation was decomposed by hydrogen sulphide.

2,9-Dimethyl-1,10-phenanthroline is a white crystalline solid, mp. 158–160 °C (uncorr.), (loc. cit., Case 160–161 °C; Geigy 160–161 °C). It is sparingly soluble in cold water, but somewhat more soluble in hot water from which it crystallizes as the dihydrate. It is readily soluble in ethanol, acetone, ether, benzene, and sparingly soluble in light petroleum. An aqueous solution produces no coloration with iron(II) salts.

Of all homologues of 1,10-phenanthroline so far tested, 2,9-dimethyl-1,10-phenanthroline showed the highest fungistatic activity (Blank 1951), and has been used in a fungistatic preparation for treatment of mycotic conditions of human skin (Gysin and Hodel, see Geigy 1952).

IV. Experimental

Two reaction procedures were used:

(i) 18 g of *o*-phenylenediamine and 100 g of sodium *m*-nitrobenzenesulphonate were dissolved in 360 ml of H_2SO_4 (190 ml H_2SO_4, sp. gr. 1·84, +170 ml H_2O) and heated to about 90 °C on a water-bath. The temperature was held fairly constant while 86 g of crotonaldehyde diacetate were added, dropwise, over a period of 4 hr. The mixture was mechanically stirred. When all the crotonaldehyde diacetate had been added the mixture was heated to and held at 125 °C for 15 min, after which the mixture began to froth and heating was discontinued.

The crotonaldehyde diacetate was prepared by acetylating freshly distilled crotonaldehyde with acetic anhydride using boron trifluoride–acetic acid complex (40% BF_3) as a catalyst (Man, Sanderson, and Hauser 1950).

(ii) 40 g of arsenic(V) oxide were dissolved in 360 ml of sulphuric acid (190 ml H_2SO_4, sp. gr. 1·84, +170 ml H_2O) by heating and stirring. 18 g of *o*-phenylenediamine were then added and the mixture heated to 90 °C and maintained at this temperature, while 36 g crotonaldehyde was added, dropwise, over 4 hr. The mixture was mechanically stirred. The mixture was then heated to 125 °C for 15 min.

The reaction mixture from either procedure was allowed to cool then poured into 600 ml water. The mixture was refrigerated overnight, filtered, and made alkaline with ammonia solution (sp. gr. 0·880). A black, oily tar precipitated, which after standing ice-cold overnight was filtered.

2,9-Dimethyl-1,10-phenanthroline was extracted by boiling the tar with water (1 l.) containing 3 ml of HCl (sp. gr. 1·16), and filtered. The residue was again extracted with water (1 l.) containing 3 ml of HCl.

The extracts were (separately) evaporated to about 20 ml, 100 ml ethanol added, followed by a solution of 15 g copper(II) chloride in 100 ml ethanol. After cooling, dichloro-(2,9-dimethyl-1,10-phenanthroline)-Cu(II) was filtered off, washed with ethanol, and finally with ether.

The copper complex was suspended in dilute H_2SO_4 (10 ml H_2SO_4, sp. gr. 1·84, +200 ml H_2O) and decomposed by passing H_2S through the solution. The copper sulphide was filtered. Ammonia added to the filtrate, precipitated crude 2,9-dimethyl-1,10-phenanthroline. The crude material was purified by dissolving in ethanol, reprecipitating the Cu(II) complex by adding copper(II) chloride, and decomposing with H_2S as above. Final purifications were made by recrystallization from light petroleum and hot H_2O.

Yields of 2,9-dimethyl-1,10-phenanthroline were from 10–16%. Procedure (i) gave the higher yields but procedure (ii) uses more convenient starting materials. From water, the compound recrystallized as the dihydrate in the form of colourless needles, m.p. 158–160 °C (Found: C, 68·9; H, 6·0; H_2O, 14·7%. Calc. for $C_{14}H_{12}N_2.2H_2O$: C, 68·9; H, 6·5; H_2O, 14·8%. H_2O was lost on drying over P_2O_5 or by heating at 80 °C).

A sample recrystallized from light petroleum yielded the hemihydrate (Found: C, 77·5; H, 6·4; N, 12·9%. Calc. for $C_{14}H_{12}N_2.0{\cdot}5H_2O$: C, 77·4; H, 6·0; N, 12·9%).

The material obtained from these preparations gave no ferroin reaction but gave the cuproine test (Smith and McCurdy 1952). 2,9-Dimethyl-1,10-phenanthroline yielded a yellow crystalline picrate, soluble in hot ethanol from which it readily crystallizes (m.p. 225 °C, decomp.) on cooling (Found: C, 55·1; H, 3·6; N, 16·1%. Calc. for $C_{20}H_{15}N_5O_7$: C, 54·9; H, 3·4; N, 16·0%).

From aqueous perchloric acid, 2,9-dimethyl-1,10-phenanthroline yielded a white, crystalline perchlorate which was recrystallized from dilute perchloric acid (Found: N, 8·7%. Calc. for $C_{14}H_{13}N_2ClO_4$: N, 9·0%).

Copper(II) chloride, added to a solution of 2,9-dimethyl-1,10-phenanthroline in dilute HCl (1 ml HCl, sp. gr. 1·16, +20 ml H_2O), precipitated a yellow-green, crystalline complex (Found: Cu, 17·2; Cl, 20·2; H_2O, 5·1%. Calc. for $C_{14}H_{12}N_2CuCl_2.H_2O$: Cu, 17·6; Cl, 19·7; H_2O 5·0%).

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COLOURING MATTERS OF AUSTRALIAN PLANTS

VII. FLAVONOID GLYCOSIDES FROM EXOCARPUS CUPRESSIFORMIS LABILL.

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Summary

The foliage of *Exocarpus cupressiformis* contains dihydrokaempferol-7-rhamnoside (2·5%), kaempferol-7-rhamnoside (0·48%), kaempferol-3-rhamnobioside (0·16%), and quercetin-3-rhamnobioside (0·23%). Mannitol was also isolated and the presence of oleanolic acid (3%) was confirmed.

I. Introduction

Exocarpus cupressiformis Labill. is a semi-parasitic tree belonging to the family Santalaceae. It is reputed to be poisonous to stock but Hurst (1942) has stated that feeding tests with sheep and rabbits were inconclusive. Some earlier investigations have revealed the presence of various chemical constituents. Crowley (1945) described the isolation of a triterpene acid which was subsequently identified as oleanolic acid. Hatt, Triffett, and Wailes (1959) have reported the presence of acetylenic acids in the seeds and roots.

In the present investigation the presence of oleanolic acid has been confirmed and the foliage has also yielded mannitol and four flavonoid glycosides which have not been isolated from natural sources previously. The isolation of these flavonoids gives some significance to the patent claim (Hart and Stewart 1920) that treatment of the plant with alkali produces a dyestuff.

II. Identification of Flavonoid Glycosides

(*a*) *Kaempferol-7-rhamnoside*

This compound is hydrolysed to kaempferol and rhamnose. Its properties agree closely with those reported by Zemplén and Bognar (1941) who prepared it by partial enzymatic hydrolysis of robinin. Methylation followed by hydrolysis gives 7-hydroxy-3,4′,5-trimethoxyflavone.

(*b*) *Dihydrokaempferol-7-rhamnoside*

Hydrolysis of this glycoside gives rhamnose and dihydrokaempferol (aromadendrin). Methylation of the glycoside with diazomethane gives a dimethyl ether which, by hydrolysis and subsequent dehydrogenation, is converted into 3,7-dihydroxy-4,5-dimethoxyflavone. This last compound was previously obtained by methylation and hydrolysis of robinin (Zemplén and

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Bognar 1941). The attachment of the sugar at the 7-position is also indicated by the blue coloured solution of the glycoside in concentrated nitric acid. Rao and Seshadri (1949) have found that this is characteristic of dihydroflavonols in which the 7-hydroxyl group is substituted.

The dihydroflavonols are relatively uncommon. They have been reviewed by Gowan, Philbin, and Wheeler (1956) and by Seshadri (1959). Only four glycosides of these compounds have been reported previously, viz. taxifolin-3-rhamnoside (Shimoda, Sawada, and Fukuda 1952), taxifolin-3′-glucoside (Hergert and Goldschmid 1958), and engelitin (dihydrokaempferol-3-rhamnoside) and *iso*engelitin (Tominaga 1955). Several 7-methyl ethers have been reported, including dihydrokaempferol-7-methyl ether which has been isolated from *Eucalyptus citriodora* (Satwalekar, Gupta, and Rao 1957), *E. maculata* (Gell, Pinhey, and Ritchie 1958), and *Prunus avium* (Chopin and Pachéco 1958).

(*c*) *Quercetin-3-rhamnobioside*

Colour reactions indicate that this is a flavonol 3-glycoside. The composition and quantitative hydrolysis show the presence of two rhamnose units and, as the glycoside is readily hydrolysed to quercetin and rhamnose by 4 per cent. formic acid, all the sugar must be attached at the 3-position. This is confirmed by methylation of the glycoside followed by hydrolysis to the known 3′,4′,5,7-tetramethylquercetin.

(*d*) *Kaempferol-3-rhamnobioside*

This substance could not be crystallized but its reactions indicate that it is a kaempferol-3-glycoside. Hydrolysis with 4 per cent. formic acid gives kaempferol and rhamnose only. Methylation gives a crystalline trimethyl ether which is hydrolysed to rhamnose and the known 4′,5,7-trimethylkaempferol.

III. Discussion

The occurrence of all these glycosides together in the one plant demonstrates the highly specific processes which must be involved in their biosynthesis. Their structures and the quantities obtained make it unlikely that any of them could be artifacts.

The two rhamnobiosides appear to be unique among natural glycosides. Although two rhamnose units have been reported in the trisaccharide component of a glycoside (Briggs and Brooker 1953), a disaccharide composed of rhamnose units apparently has not been encountered previously.

Several glycosides of kaempferol which yield only rhamnose on hydrolysis have been reported in the literature. Of these kaempferitrin and " lespedin " have been identified as kaempferol-3,7-dirhamnoside (Hattori and Hasegawa 1951). Kaempferol-3-rhamnoside has been isolated by King and Acheson (1950) who found it in *Afzelia* spp. and named it afzelin. It had been reported previously as a constituent of *Trifolium pratense* and named trifolin, but Hattori, Hasegawa, and Shimokoriyama (1943) have stated that the latter is a galactoside. The remaining kaempferol rhamnosides have not been fully characterized. Petrie (1924) established the nature of the hydrolysis products from a constituent

of an *Acacia* sp., but the structure of the glycoside was not determined. A compound isolated by Kobayashi (1944) from *Onychium japonicum* gave kaempferol and two molecules of rhamnose. Its constitution was not determined but its properties suggest that it may have been kaempferitrin. Similarly an unidentified glycoside extracted from *Pueraria hirsuta* by Ohira (1933) may have been kaempferitrin.

Apparently quercitrin (the 3-rhamnoside) and one other product (Ice and Wender 1953) are the only previously known glycosides of quercetin which have rhamnose as the sole sugar component.

Hattori (1926) claimed that the glycoside acaciin from *Robinia pseudacacia* is a rhamnobioside of acacetin (4'-methoxy-5,7-dihydroxyflavone). However, McIlroy (1953) identifies acaciin with linarin, which was isolated by Merz and Wu (1936) from *Linaris vulgaris*, and gives acacetin, rhamnose, and glucose as the products of hydrolysis.

IV. Experimental

All melting points are corrected and were observed in sealed Pyrex capillaries. Light petroleum refers to the fraction with boiling range 50–70 °C. Microanalyses are by Dr. K. W. Zimmermann and assistants.

(*a*) *Extraction.*—The plant was collected on the Mornington Peninsula, Victoria, and the milled, air-dried leaves and branchlets (1·64 kg; 7% moisture) were extracted successively with light petroleum, acetone, water, and methanol. The light petroleum extract contained waxes which were discarded. The acetone extract was evaporated to dryness and the residue was exhaustively extracted with ether. The dark green ethereal solution was concentrated and then shaken repeatedly with aqueous sodium hydroxide (5%) until there was no further separation of a sparingly-soluble sodium salt. The salt was collected, dissolved in boiling 50% ethanol, treated with charcoal, and acidified with concentrated hydrochloric acid to yield almost pure oleanolic acid (45·7 g). The remaining aqueous and ethereal solutions contained only traces of gum. The ether-insoluble material was extracted repeatedly with hot water (80 °C; total volume 2 l.) leaving dihydrokaempferol-7-rhamnoside (38 g) as a pale green, insoluble solid. The aqueous solution was concentrated to about 100 c.c. (reduced pressure) and extracted with ethyl acetate. The remaining aqueous solution contained only small traces of flavonoid and was discarded. The material from the ethyl acetate (a brown gum) was examined by paper chromatography on Whatman No. 1 paper by the ascending method in acetic acid, hydrochloric acid, water (30 : 3 : 10). The flavonoids were located on the paper by examination under ultraviolet light and by spraying with Fehling's solution. Three components with R_F values 0·80, 0·82, and 0·85 were detected. The mixture was dissolved in ethanol and fractionally precipitated with neutral lead acetate. The first small precipitate contained much brown impurity, but little flavonoid, and was discarded. The second precipitate was separated by centrifuging and the remaining solution was precipitated with basic lead acetate.

The neutral lead acetate precipitate was decomposed with hydrogen sulphide to give quercetin-3-rhamnobioside (3·6 g) as a pale yellow gum. Similar treatment of the basic lead acetate precipitate gave a gum which on trituration with methanol was separated into a yellow insoluble crystalline fraction, kaempferol-7-rhamnoside (1·9 g), and a methanol soluble gum containing the kaempferol-3-rhamnobioside (2·5 g).

The aqueous extract from the plant was concentrated to small volume under reduced pressure and then extracted with ethyl acetate. Evaporation of this extract gave more kaempferol-7-rhamnoside (1·4 g). The aqueous solution was then evaporated to dryness, the residue was dissolved in ethanol, and the crystalline material (2·5 g) which slowly separated was identified as mannitol.

The methanol extract also gave kaempferol-7-rhamnoside (4·0 g) and a small quantity of mannitol.

(*b*) *Oleanolic Acid.*—The acid separated from methanol as needles, m.p. 308–309 °C, $[\alpha]_D^{21}$ +77·1±0·5° (*c*, 0·92 in chloroform) (Found: C, 79·0; H, 10·6%. Calc. for $C_{30}H_{48}O_3$: C, 78·9; H, 10·6%). The acetate crystallized from methanol as needles, m.p. 265–265·5 °C, and the methyl ester separated from methanol as fluffy needles, m.p. 200·5–201 °C.

Anstee *et al.* (1952) report m.p. 309–312 °C, $[\alpha]_D^{15}$ +80° (*c*, 0·93 in chloroform) for oleanolic acid; m.p. 267–268 °C for the acetate; m.p. 201 °C for the methyl ester.

(*c*) *Kaempferol-7-rhamnoside.*—The product was crystallized from methanol as fine yellow needles, m.p. 221–222 °C (Found: C, 57·8; H, 4·8%. Calc. for $C_{21}H_{20}O_{10}$: C, 58·3; H, 4·7%). It gave an orange colour with magnesium and hydrochloric acid in alcohol but no colour by zinc reduction. The R_F value in the system described above was 0·82. Concentration of the mother liquors gave material of dissimilar appearance but the same melting point and R_F value. Analysis showed this to be a hydrate (Found: C, 56·3; H, 5·0%. Calc. for $C_{21}H_{20}O_{10}.H_2O$: C, 56·0; H, 4·9%). Zemplén and Gerecs (1935) report m.p. 230 °C (decomp.).

Hydrolysis of the glycoside gave kaempferol as pale yellow needles from aqueous ethanol, m.p. 280–280·5 °C (Found: C, 62·6; H, 3·6%. Calc. for $C_{15}H_{10}O_6$: C, 62·9; H, 3·5%). Kaempferol tetra-acetate crystallized from methanol as needles, m.p. 117–118 °C, solidifying and remelting at 185·5–186·5 °C (Found: C, 60·6; H, 4·3; CH_3CO, 37·1%. Calc. for $C_{23}H_{18}O_{10}$: C, 60·8; H, 4·0; 4×CH_3CO, 37·9%). Hillis (1952) reports m.p. 279 °C for kaempferol and m.p. 180–181 °C for its tetra-acetate. Hattori, Hasegawa, and Shimokoriyama (1943) give m.p. 116–120 °C and 186 °C for the latter.

Paper chromatography of the hydrolysate showed the presence of rhamnose. Whatman No. 4 paper was used and two different solvent systems: ethyl acetate–pyridine–water (12 : 5 : 4) and *iso*propanol–water (4 : 1). The sugar was located by spraying with aniline phthalate.

The glycoside was methylated with a large excess of diazomethane in methanol–ether. After 24 hr the methyl ether was collected and crystallized from methanol in needles, m.p. 254–254·5 °C (Found: OMe, 18·7%. Calc. for $C_{24}H_{26}O_{10}$: C×OMe, 19·6%). Zemplén and Bognar (1941) report m.p. 251 °C.

Hydrolysis of the methylated glycoside gave 7-hydroxy-3,4′,5-trimethoxyflavone which formed needles from methanol, m.p. 292–292·5 °C (Found: C, 66·0; H, 5·0; OMe, 28·2%. Calc. for $C_{18}H_{16}O_6$: C, 65·8; H, 4·9; 3×OMe, 28·3%). The acetate crystallized from methanol as needles, m.p. 158–159 °C. Zemplén and Bognar (1941) report m.p. 289–290 °C for 7-hydroxy-3,4′,5-trimethoxyflavone and m.p. 157·5–158 °C for the acetate.

(*d*) *Dihydrokaempferol-7-rhamnoside.*—The crude product was washed with ether and crystallized first from water and then from aqueous methanol at room temperature. The *glycoside* was obtained as needles, m.p. 160–161 °C (decomp.). After drying at 100 °C in a vacuum over phosphorus pentoxide the melting point was raised to 165–166 °C, $[\alpha]_D^{21}$ −99·0±0·3° (*c*, 2·0 in ethanol) (Found: C, 57·2; H, 5·4%. Calc. for $C_{21}H_{22}O_{10}.\frac{1}{2}H_2O$: C, 56·8; H, 5·2%). It gave a magenta colour with both magnesium and zinc in alcoholic hydrochloric acid, and a blue colour with concentrated nitric acid.

Hydrolysis with boiling 3% sulphuric acid gave dihydrokaempferol, needles from aqueous methanol at room temperature, m.p. 242–243 °C, $[\alpha]_D^{23}$ +47·3±0·3° (*c*, 1·7 in 1 : 1 acetone–water (Found: C, 62·8; H, 4·3; O, 33·3%. Calc. for $C_{15}H_{12}O_6$: C, 62·5; H, 4·2; O, 33·3%). It gave an orange-red colour with magnesium-hydrochloric acid, a red colour with zinc-hydrochloric acid, and a brown colour with nitric acid. The R_F value was 0·91 in the system described in Section IV (*a*). Pew (1948) reports m.p. 237–241 °C, $[\alpha]_D$ +45°; Hillis (1952) gives m.p. 247–248·5 °C, $[\alpha]_D^{25}$ +51·5° (*c*, 2 in 1 : 1 acetone–water); Brewerton (1956) gives m.p. 240–242 °C.

The hydrolysate was neutralized with solid barium carbonate, filtered, and the filtrate was evaporated to dryness under reduced pressure. Rhamnose was identified by preparation of the osazone (m.p. and mixed m.p.) and by paper chromatography as described in Section IV (*c*).

The dihydrokaempferol (200 mg), anhydrous potassium acetate (400 mg), and acetic acid (2 c.c.) were heated under a reflux condenser and iodine (200 mg) was added during 1 hr. After a total heating time of 2 hr, the solvent was removed (reduced pressure), the residue was tri-

turated with saturated aqueous sulphur dioxide solution, and the product (160 mg) was collected. Crystallization from aqueous ethanol gave pale yellow needles, m.p. 280–280·5 °C, alone or mixed with the kaempferol described in Section IV (*c*). The R_F value was 0·61.

The glycoside was allowed to react overnight with a large excess of diazomethane in methanol-ether. The *dimethyl ether* separated as cream needles (70% yield). Crystallization from methanol gave needles, m.p. 231–232 °C (Found: C, 59·5; H, 5·8; OMe, 13·7%. Calc. for $C_{23}H_{26}O_{10}$: C, 59·7; H, 5·7; 2×OMe, 13·4%). Hydrolysis with dilute sulphuric acid gave *3,7-dihydroxy-4′,5-dimethoxyflavanone* which formed needles from methanol, m.p. 237–237·5 °C (Found: C, 64·6; H, 5·1%. Calc. for $C_{17}H_{16}O_6$: C, 64·6; H, 5·1%). Dehydrogenation of this product with iodine and potassium acetate in acetic acid gave 3,7-dihydroxy-4′,5-dimethoxyflavone, yellow prisms from methanol, m.p. 315–316 °C. The diacetate crystallized from methanol as needles, m.p. 192–193 °C. Zemplén and Bognar (1941) report m.p. 316–318 °C for the flavone and m.p. 192–193 °C for its acetate.

(*e*) *Quercetin-3-rhamnobioside.*—The crude resinous product was dissolved in a small volume of hot water and allowed to stand in the refrigerator for 7 days. A pale yellow precipitate separated and a second crop was obtained from the mother liquors. This material was crystallized from water to give yellow needles of indefinite melting point. When dried at 110 °C over phosphorus pentoxide in a vacuum for 10 hr the *glycoside* had m.p. 179–180 °C (Found: C, 54·6; H, 5·0%. Calc. for $C_{27}H_{30}O_{15}$: C, 54·9; H, 5·0%). It gave a deep orange colour with magnesium, and with zinc, in the presence of hydrochloric acid. Paper chromatography of the glycoside and mother liquors indicated the presence of only one flavonoid with R_F 0·80. The dried glycoside (287 mg) was heated on the water-bath with sulphuric acid (6 c.c. of 2%) for 30 min. The aglycon (137 mg) was collected and dried to constant weight (Found: quercetin, 48·1%. Calc. for $C_{27}H_{30}O_{15}$: quercetin, 49·5%). The quercetin crystallized from aqueous ethanol as fine yellow needles, m.p. 315–316 °C, alone or mixed with an authentic specimen. Both samples had R_F 0·48 (Found: C, 59·5; H, 3·5%. Calc. for $C_{15}H_{10}O_7$: C, 59·6; H, 3·3%). The penta-acetate had m.p. 196–196·5 °C, alone or mixed with authentic material.

The hydrolysate, after neutralization and concentration, gave a single spot corresponding to rhamnose on a paper chromatogram prepared as in Section IV (*c*).

The glycoside was methylated with a large excess of diazomethane in ether-methanol until the product no longer gave a colour with ferric chloride. Hydrolysis of the resulting gum gave pale yellow needles, m.p. 194–195 °C. Crystallization from benzene gave the pure 3-hydroxy-3′,4′,5,7-tetramethoxyflavone as fine needles, m.p. 198–198·5 °C, which acquired a yellow colour on exposure to air (Found: C, 63·7; H, 5·0; OMe, 32·5%. Calc. for $C_{19}H_{18}O_7$: C, 63·7; H, 5·1; 4×OMe, 34·6%). The acetate crystallized from methanol as needles, m.p. 163–164 °C. Kostanecki, Lampe, and Tambor (1904) report m.p. 197–198 °C, and Ice and Wender (1953) give m.p. 195–196 °C. Attree and Perkin (1927) find m.p. 160–162 °C for the acetate.

(*f*) *Kaempferol-3-rhamnobioside.*—Several attempts to crystallize this product were unsuccessful. It gave an orange-red colour with magnesium and hydrochloric acid and a rose colour by zinc reduction. Paper chromatography as in Section IV (*a*) showed only a single flavonoid with R_F 0·85. Hydrolysis of the glycoside gave kaempferol.

The glycoside was methylated as described in Section IV (*e*); the resulting gum was dissolved in the minimum volume of hot water, and the solution was cooled and shaken with an equal volume of ether. The solid product was crystallized from aqueous methanol to give the *trimethyl ether* as needles, m.p. 243–243·5 °C (Found: C, 58·2; H, 6·0%. Calc. for $C_{20}H_{20}O_{14}$: C, 58·1; H, 5·9%).

Hydrolysis of this product gave 3-hydroxy-4′,5,7-trimethoxyflavone which formed needles from methanol, m.p. 149–150 °C (Found: C, 65·9; H, 5·0; OMe, 27·9%. Calc. for $C_{18}H_{16}O_6$: C, 65·8; H, 4·9; 3×OMe, 28·3%). The acetate crystallized from methanol as needles, m.p. 192–193 °C. Nakaoki (1943) and Fukuchi and Imai (1950) have reported m.p. 148–150 °C for the flavone. It is described as pale yellow needles, m.p. 151 °C, by King and Acheson (1950) and according to Tominaga (1955) its acetate has m.p. 185–186 °C.

Paper chromatography as in Section IV (*c*) again showed the presence of rhamnose in the filtrate after hydrolysis.

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COMPARATIVE STUDIES OF BROWN COAL AND LIGNIN

I. INFRA-RED SPECTRA

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Summary

The infra-red spectra of two softwood lignins are discussed with reference to the spectra of their acetyl and methoxyl derivatives. The spectra of the respective acetyl derivatives provide conclusive evidence for the presence of both phenolic and alcoholic groups in lignin and oxidized lignin, and of alcoholic groups only in the methoxyl derivatives of both these samples. Treatment of lignin with hydriodic acid in the conventional Zeisel determination of methoxyl groups eliminates the alcoholic hydroxyl groups and appears to split aliphatic ether linkages. The spectrum of lignin treated with hydriodic acid is very similar to that of brown coal, which supports previous chemical evidence that brown coal appears to be essentially " demethylated dehydrated lignin ". The progress of the isolation of lignin from wood was followed by infra-red spectroscopy.

I. INTRODUCTION

Although the chemical origin of coal is still uncertain and both lignin and cellulose have been postulated as the parent materials (Fischer and Schrader 1922; Enders 1943; Gillet 1955), Brooks and Sternhell (1957) recently noted a simple relation between the composition and functional-group analyses of Victorian brown coals and of lignin; the former appear to be demethylated, dehydrated lignin. This relation is considered further in the present paper where the infra-red spectra of brown coal, lignin, and some of their chemical derivatives are discussed and compared.

II. EXPERIMENTAL

(*a*) *Sources of Materials*

The sample of acid-washed brown coal used (from the Yallourn seam) was identical with that described by Durie and Sternhell (1958).

The cellulose sample was acetylation grade cotton linters, supplied by C.S.R. Chemicals Pty. Ltd., Sydney.

Two preparations of softwood lignin (designated lignin I and lignin II) were used. Lignin I (a hydrochloric acid lignin) was obtained from a sample of Douglas fir using modifications of the methods of Halse (1924) and Urban (1926).

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Lignin II (a Klason lignin) was prepared by sulphuric acid extraction of a sample of Pacific maple (cf. Campbell and McDonald 1952). Elementary analyses and functional-group contents of the lignin samples are given in Table 1, and the functional-group contents of some chemically modified lignin derivatives are given in Table 2.

TABLE 1

ELEMENTARY ANALYSES AND FUNCTIONAL-GROUP CONTENTS OF THE LIGNINS

Dry ash-free basis

	C (%)	H (%)	O (%)	Methoxyl Content		Total Acidity (m-equiv/g)	Carboxylic Acidity (m-equiv/g)
				(%)	(m-equiv/g)		
Lignin I ..	65·5	5·6	—	14·3	4·60	2·94	
Lignin II ..	65·3	5·4	28·8	16·0	5·15	3·30	0·52

TABLE 2

FUNCTIONAL-GROUP CONTENTS OF THE CHEMICALLY MODIFIED LIGNINS

m-equiv/g, dry ash-free basis unless otherwise stated

Group Content	Lignin I	Lignin II	HI-Treated Lignin I*	HI-Treated Lignin II†	Lignin II Oxidized with Oxygen and Alkali‡
Methoxyl content (%)	14·3	16·0	—	—	15·3
Methoxyl content of methylated sample (%)	18·5	26·6	16·7	14·1	25·7
(m-equiv/g, on original lignin basis)		9·75			
Hydroxyl by methylation (original lignin basis)		11·1			
Acetyl content of acetylated sample	4·89	5·33	6·25	—	—
Hydroxyl by acetylation	6·15	6·86	8·45	—	—
Acetyl content of methylated sample, subsequently acetylated ..	—	2·87	—	0·67	—
Hydroxyl content corresponding to preceding item		3·27		0·94	
Methoxyl content of methylated acetylated sample		22·8		11·7	

* Elementary analysis: C, 65·7; H, 4·8% (dry ash-free basis).

† Total acidity 9·17 m-equiv/g.

‡ Carboxylic acidity 1·43 m-equiv/g, total acidity 4·35 m-equiv/g; on HI-treatment, the product had total acidity 8·73 m-equiv/g and carboxylic acidity 1·62 m-equiv/g.

(*b*) *Estimation of Functional Groups*

(i) Total acidity was determined by the baryta absorption method (Brooks and Sternhell 1957).

(ii) Carboxylic acidity was determined by the acetate-exchange technique, as modified by Lynch *et al.* (1959).

(iii) Hydroxyl groups were estimated by acetylation followed by hydrolysis, as described by Brooks, Durie, and Sternhell (1958*b*).

(iv) Methoxyl contents were determined by the Zeisel method.

(*c*) *Chemical Modification of the Lignins*

(i) Acetylations were performed using acetic anhydride and pyridine (Brooks, Durie, and Sternhell 1958*b*).

(ii) Hydriodic acid treatment (demethylation) was performed as follows: The lignin was heated under reflux with a large excess of hydriodic acid (density 1·7 g/c.c.) under nitrogen (1 hr). The mixture was diluted and the residue was collected and washed thoroughly, then dried (under reduced pressure) at 100 °C.

(iii) Methylations were performed using a large excess of diazomethane in ether/methanol (10 : 1). Several successive treatments were employed and reactions were carried out below 5 °C to minimize thermal decomposition of the diazomethane to polymethylene.

(iv) Oxidation: The lignin (3 g) was shaken for 15 hr under oxygen in the presence of 1N sodium hydroxide (150 ml). The sample was acidified, filtered off, and washed thoroughly, then dried under reduced pressure at 100 °C.

(*d*) *Infra-Red Spectra*

These were obtained using the potassium halide disk technique and a Perkin-Elmer Model 21 double-beam spectrophotometer (rock-salt prism). The conditions for sample and disk preparation were as described by Brooks, Durie, and Sternhell (1958*a*).

III. Results and Discussion

(*a*) *Spectra of Lignin and Its Derivatives* (*Figs. 1 and 2*)*

The infra-red spectra of various lignins appear in the literature (e.g. Jones 1948, 1949; Freudenberg *et al.* 1950; Schubert and Nord 1950; Kudzin, de Baun and Nord 1951; Kudzin and Nord 1951; Kratzl and Tschamler 1952; Ekman 1957), but these spectra have been used largely for qualitative comparison of lignins of different origin.

Examination of the changes that occur in the spectrum of lignin as a result of controlled chemical modifications (e.g., acetylation, methylation, oxidation, treatment with hydriodic acid) permits a more detailed interpretation of the lignin spectrum in terms of the chemical structures present than any previously attempted.

* In the present study some differences were observed in the spectra of the two lignin preparations (cf. Fig. 1) but the discussion that follows is applicable equally to both lignins unless otherwise stated.

(i) *Absorption Features Characteristic of Aliphatic Structures.*—Absorption bands at 2920, 2830, and 1465 cm^{-1} in the spectrum of lignin establish the presence of aliphatic structures and are consistent with the presence of methylene ($-CH_2-$) and methoxyl ($-OCH_3$) groups. The increase in the intensity of these bands, in particular the 2830 cm^{-1} bands, following methylation of the lignin substantiates their correlation, in part at least, with methoxyl groups attached to an aromatic nucleus (cf. Henbest *et al.* 1957 ; Bellamy 1958, p. 16 ; Durie and Shannon 1958).

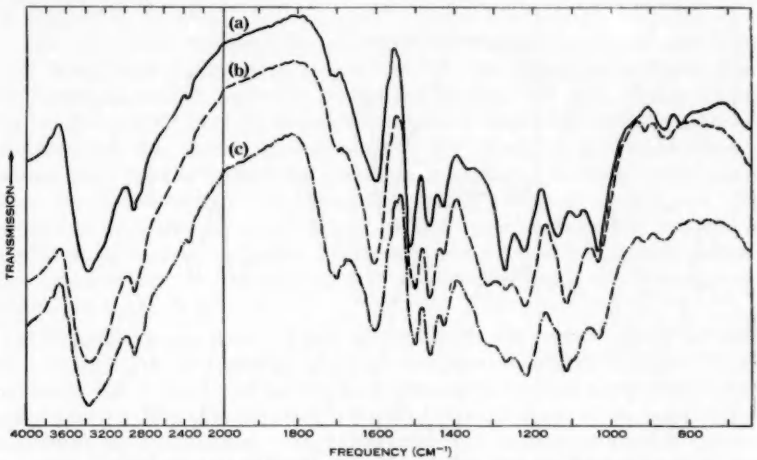

Fig. 1.—Comparison of the infra-red spectra of (*a*) hydrochloric acid lignin from Douglas fir (lignin I) ; (*b*) sulphuric acid (Klason) lignin from Pacific maple (lignin II) ; (*c*) lignin II after mild alkaline oxidation.

The band near 1425 cm^{-1} in the spectrum of lignin also increased in intensity (accompanied by a slight shift to near 1415 cm^{-1}) on methylation of the lignin and it disappeared on treatment of the lignin with hydriodic acid (i.e. demethylation). This behaviour indicates that the 1425 cm^{-1} lignin band arises from the CH_3 symmetrical bending vibration in the methoxyl (OCH_3) group.

The pronounced band near 1465 cm^{-1} in the lignin spectrum increases in intensity on methylation of the lignin and appears slightly shifted at 1455 cm^{-1} in the spectrum of " demethylated " lignin, indicating that both $-CH_2-$ (bending vibration) and $-OCH_3$ (symmetrical bending vibration) groups are contributing to this 1465 cm^{-1} band.

The absence of discrete absorption near 1380 cm^{-1}, characteristic of terminal C-methyl groups (cf. Bellamy 1958), and near 720 cm^{-1}, characteristic of methylene chains, $(CH_2)_n$ (where $n>4$), shows that these structures do not contribute significantly to the structure of lignin.

The lignin spectrum provides no evidence for the presence of non-conjugated ethylenic structures ; however, the absorption intensity due to the stretching

vibration of non-conjugated olefinic groups is highly dependent on the position of such linkages in the molecule and is negligible if there is symmetry, or pseudo-symmetry, about the linkage (Jones and Sandorfy 1956 ; Bellamy 1958).

(ii) *Absorption Characteristic of Aromatic Structures.*—Two strong absorption bands near 1600 cm^{-1} and near 1500 cm^{-1} in the spectra of lignins are probably associated with aromatic ring vibrations and thus provide evidence for the presence of aromatic nuclei in lignin (Kratzl and Tschamler 1952). The relative intensity and positions of these two bands appear to change slightly depending

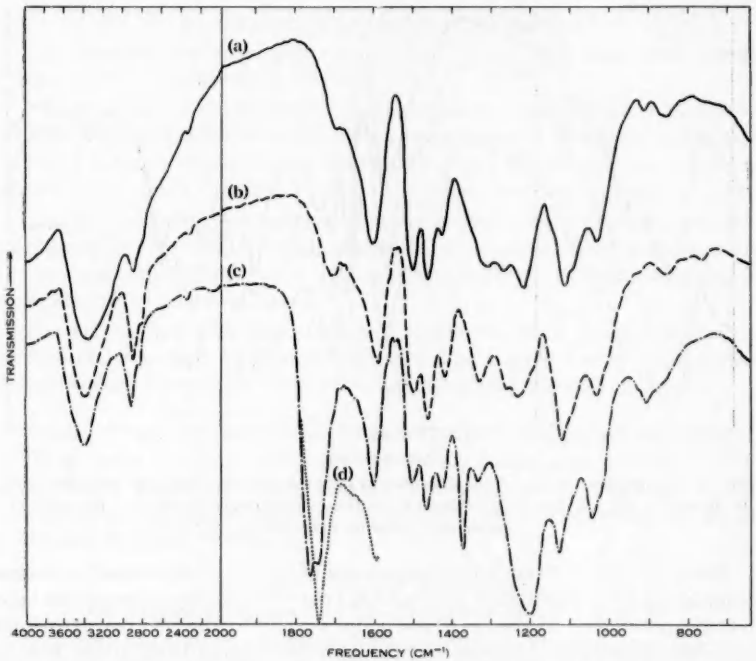

Fig. 2.—Comparison of the infra-red spectra of (*a*) lignin II ; (*b*) lignin II after methylation ; (*c*) lignin II after acetylation ; and (*d*) lignin II after methylation then acetylation.

on the origin (and mode of isolation ?) of the lignin. Thus the band near 1500 cm^{-1} appears at 1510 cm^{-1} for lignin I and 1502 cm^{-1} for lignin II and is sharper and usually more intense (peak) than the bands near 1600 cm^{-1}. The latter band (at 1595 cm^{-1} for lignin I and 1607 cm^{-1} for lignin II) is broader relative to the 1500 cm^{-1} band than is normal for simple substituted aromatic structures and shows definite asymmetry on the high-frequency side. The absence of a band near 3030 cm^{-1} and the presence of only very weak absorption between 900 and 700 cm^{-1} (815 and 855 cm^{-1}—lignin I ; and 855 and 910 cm^{-1}—lignin II) show that the aromatic rings are highly, although probably not completely, substituted. The variable presence of nuclei with isolated (855 cm^{-1})

and two or three adjacent (815 cm^{-1}) unsubstituted positions is suggested (Bellamy 1958, p. 65).

Slight changes occurred in the position of the aromatic band near 1600 cm^{-1} as a result of chemical modification. Thus methylation of the lignin resulted in a decrease in frequency of 10 to 15 cm^{-1}. The position of the band near 1500 cm^{-1} did not alter on methylation or treatment with hydriodic acid but, as will be discussed below, considerable changes in intensity followed the latter treatment. The intensity and positions of the bands characteristic of aromatic ring vibrations are known to be affected by the type and position of substituents (Bellamy 1958, p. 23).

(iii) *Absorption Characteristic of Oxygen-Containing Groups.*—A very strong broad band with a maximum at 3380 cm^{-1} in the spectrum of lignin shows that hydrogen-bonded hydroxyl groups are present. A considerable fraction of these groups, but not all, are reactive to methylation and the appearance on acetylation of two acetate carbonyl bands (Fig. 2 (*c*)) at 1765 cm^{-1} (phenolic acetate) and 1740 cm^{-1} (alcoholic acetate) (cf. Jones and Sandorfy 1956, p. 482) shows that both phenolic and alcoholic hydroxyl groups occur in lignin. The presence of alcoholic hydroxyl groups, which resist methylation but can be acetylated, is further confirmed by the presence of a single acetate carbonyl band at 1740 cm^{-1} in the spectrum of the product from the acetylation of methylated lignin (Fig. 2 (*d*)).

The lignin spectra show complex absorption in the region 1400 to 950 cm^{-1}, where saturated oxygen-containing groups are known to absorb strongly. Marked qualitative and quantitative differences were observed in this region with the two lignins studied (Fig. 1), probably reflecting the different origin and mode of isolation of the two samples. Structural diagnosis based only on this region of the spectrum must be made with extreme caution in the absence of supporting evidence, since most substances exhibit non-assignable skeletal (or " fingerprint ") vibrations in this region. However, in the present study of lignin the strong discrete absorption that occurs over the region 1400 to 950 cm^{-1} can be associated with reasonable certainty with the presence of oxygen groups since, under the conditions used to observe the spectra, only weak absorption is observed in this region for aromatic and paraffinic structures. Also, since chemical evidence, and evidence from other regions of the spectra, confirm the presence in lignin of phenolic, alcoholic, and methoxyl groups and the virtual absence of carbonyl groups (ketonic or carboxylic), reasonable class assignments to specific bands in the 1400 to 950 cm^{-1} region can be attempted. This is assisted by the changes that occur in these bands as a result of controlled chemical modifications of the oxygen-containing functional groups.

The spectra of both lignins studied showed strong bands at 1265, 1215, and 1030 cm^{-1}. In addition lignin I showed a strong band at 1130 cm^{-1} and lignin II strong bands at 1320 and 1115 cm^{-1}.

The 1265 and 1215 cm^{-1} bands are assignable to phenoxy groups (=C—O asymmetrical stretching vibrations : Jones and Sandorfy 1956, p. 435). Methylation of lignin or oxidized lignins had little effect on the former band and resulted in a slight shift to 1230 cm^{-1} of the 1215 cm^{-1} band, suggesting a more specific

assignment to phenolic ether (1265 cm^{-1}) and phenolic hydroxyl groups (1215 cm^{-1}).

A general decrease in absorption near 1300 cm^{-1} in the spectra of the lignins and oxidized lignins on methylation or acetylation indicates that the in-plane-deformation vibrations of hydrogen-bonded phenolic hydroxyl groups are absorbing here without resulting in a specific peak.

The bands at 1130 cm^{-1} (lignin I), 1115 cm^{-1} (lignin II), and 1030 cm^{-1} (lignins I and II) can be assigned with less certainty although these are all probably associated with C—O stretching vibrations in aliphatic ethers and alcohols. The 1130 cm^{-1} lignin I band is unaffected by methylation and disappears on acetylation, which is consistent with the presence of secondary or tertiary alcoholic groups in this lignin (cf. Freudenberg, Sohns, and Janson 1935; Brauns 1952, p. 249). The 1115 cm^{-1} lignin II (and oxidized lignin II) band, on the other hand, increased slightly in intensity, or was overlapped by a new band, on methylation, and was unchanged by acetylation of the lignin, suggesting an assignment to ether linkages, in particular to the symmetrical C—O stretching vibrations in mixed methyl-aryl ethers. Against this is the absence of a similar behaviour for lignin I, which must also contain methoxyl groups attached to aromatic nuclei (particularly in the methylated sample). The 1030 cm^{-1} band in the spectra of both lignins, which was unaffected by methylation and masked by acetate group features (see below) on acetylation, is probably assignable to primary alcohol or aliphatic ether groups.

The only infra-red evidence for the presence of carbonyl groups in the lignins studied was a weak band at 1700 cm^{-1} (sodium acetate exchange with lignin II (cf. Table 2) suggests presence of 0·5 m-equiv/g of —COOH groups). There was a pronounced carbonyl band at 1700 cm^{-1} in the spectrum of oxidized lignin II (sodium acetate exchange indicated 1·43 m-equiv/g of —COOH groups) but oxidation was insufficient to affect the characteristic lignin II absorption in the 1400 to 950 cm^{-1} region (cf. Fig. 1). The published spectra of lignin often exhibit strong absorption near 1700 cm^{-1} (see, for example, Kudzin and Nord 1951).

In acetylated lignins and acetylated methylated lignins, in addition to the carbonyl frequencies already mentioned (Section III (*a*) (iii)), other features all of which are characteristic of the acetate group (Durie and Sternhell 1959; Brooks, Durie, and Sternhell 1958*a*) appear in the spectra at 1370 cm^{-1} ($C—CH_3$), 1220 cm^{-1} (C—O in alcoholic acetate groups), 1190 cm^{-1} (C—O in phenolic acetate groups), 1040, 1015, and 900 cm^{-1}.

(*b*) *Lignin the Precursor of Brown Coal* (*Fig. 3*)?

The infra-red spectra of Victorian brown coals have been discussed (Brooks, Durie, and Sternhell 1958*a*). The main differences between the spectra of lignin and of brown coals (see Figs. 2 and 3) are:

(i) In the 1600 to 1500 cm^{-1} (aromatic ring vibration) region lignin has a strong sharp band near 1500 cm^{-1} in addition to a strong 1600 cm^{-1} band, while brown coal has a single very strong band near 1600 cm^{-1} with only a shoulder, or inflexion, evident near 1500 cm^{-1}.

(ii) Lignin has two distinct bands at 1460 and 1425 cm^{-1} (aliphatic CH in-plane deformation) compared with a single broad band near 1450 cm^{-1} for brown coals.

(iii) Both lignin and brown coal have strong absorption over the range 1400 to 950 cm^{-1}. With lignin several pronounced bands appear (at 1365, 1265, 1215, 1130, 1090, and 1030 cm^{-1} for lignin I; and at 1320, 1265, 1215 (1090), and 1030 cm^{-1} for lignin II); with brown coals there is a broad band of unresolved absorption with vague maxima near 1270 and 1220 cm^{-1}.

(iv) Brown coal has appreciable discrete absorption at 1700 cm^{-1} (carboxyl C=O groups). This type of absorption was very weak for the lignins studied.

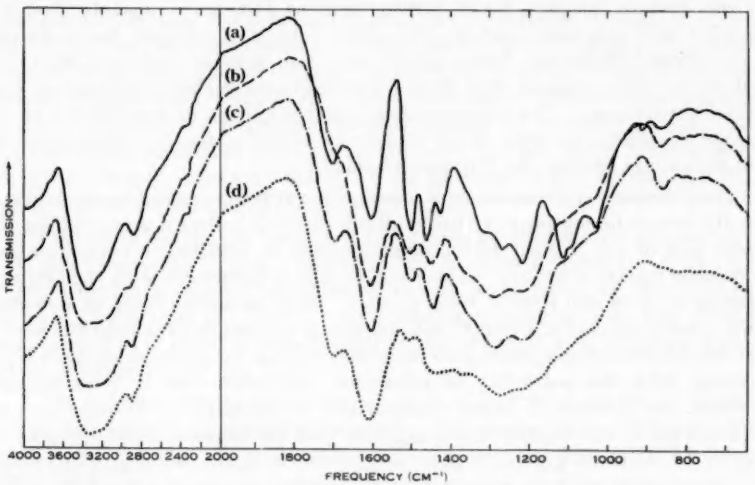

Fig. 3.—Comparison of the infra-red spectra of (*a*) lignin II after mild alkaline oxidation; (*b*) lignin II treated with HI; (*c*) sample (*a*) treated with HI; and (*d*) brown coal (Yallourn).

The spectrum of the oxidized lignin, apart from the presence of pronounced carboxylic carbonyl group absorption at 1700 cm^{-1}, showed similar differences from the spectra of brown coals.

Treatment of the lignin and oxidized lignin with hydriodic acid (HI) resulted in spectacular changes in the infra-red spectra of both samples. The modified spectra (Fig. 3) resembled very closely the spectra of brown coals, apart from the virtual absence of carbonyl absorption near 1700 cm^{-1} in the case of the HI-treated lignin. Thus there was a marked decrease in the intensity of the band near 1500 cm^{-1}, which became a weak feature relative to the very strong band near 1600 cm^{-1}. The lignin bands at 1460 and 1425 cm^{-1} were replaced by a single band near 1450 cm^{-1} similar to that in the spectra of brown coals. The discrete lignin absorption between 1400 and 950 cm^{-1} was replaced by a broad band of unresolved absorption with broad maxima near 1260 and 1220 cm^{-1}.

The procedure employed for the HI treatment of the lignin (and oxidized lignin) was identical with that normally used in determining the methoxyl content, and should therefore result in complete demethylation. However, the hydroxyl content of the HI-treated lignin (8·45 or 7·90 m-equiv/g when corrected to a " lignin basis " for lignin I) was found to be less than the combined hydroxyl and methoxyl contents of the lignin (10·75 m-equiv/g for lignin I). The elementary composition (C, 65·7 ; H, 4·8% for lignin I) also was somewhat different from that calculated from a simple demethylation of lignin (that is, C, 64·2 ; H, 5·1% for lignin I).

The infra-red spectra indicate that changes other than simple demethylation occur on HI-treatment of lignin. Whereas the spectrum of acetylated lignin has two acetate carbonyl bands, which occur at 1765 cm^{-1} (phenolic acetate) and 1735 cm^{-1} (alcoholic acetate), the latter being the stronger, the spectrum of acetylated HI-treated lignin shows only one acetate carbonyl band (at 1770 cm^{-1}). This suggests that there are virtually no alcoholic hydroxyl groups in the treated lignin. The disappearance from the spectra of the aliphatic C—O features on treatment with HI is additional evidence for the elimination of alcoholic groups during the " demethylation ".

Thus chemical and spectroscopic observations strongly suggest that treatment with HI effects elimination of virtually all the alcoholic hydroxyl groups originally present and of any formed during demethylation in addition to demethylation of aromatic methoxyl groups. This conclusion is in agreement with the findings of earlier workers (see Brauns 1952, p. 432). Since no iodine could be detected in the treated lignin (cf. Brauns 1952, p. 431) it is possible that dehydration to form ethylenic structures (there is no infra-red evidence for these) could have been occurring, with the possibility of subsequent saturation due to cross-linkage. Moreover, the absence of bands characteristic of aliphatic C—O structures in the spectrum of the treated lignin suggests that all aliphatic ether linkages in addition to methoxyl groups, if these are present in lignin, are also split by the HI. Elementary analyses suggest that in addition to loss of $CH_2(OCH_3 \rightarrow OH)$ there has been the loss of 5 moles of water and 2 moles of hydrogen per 200 carbon atoms (lignin I).

Comparison of the actual elementary composition of the HI-treated lignin I with the elementary composition calculated on the assumption that all the methoxyl groups in the lignin are split and that the decrease in hydroxyl content noted previously (Section III (*a*) (iii)) is due to loss of alcoholic hydroxyl groups as water (the " lignin basis " weight factor being calculated by successive approximations) again shows that hydrogen in excess of that which may be evolved as water is lost.

The foregoing evidence lends support to the suggestion (Brooks and Sternhell 1957) that there is a comparatively simple chemical relationship between lignin and Victorian brown coals, namely that these brown coals are essentially demethylated, dehydrated lignin. If this is so, the net result of natural agencies acting on vegetable deposits, assisted by the geological time factor, is similar to that produced in the laboratory by mild oxidation and treatment with HI. The absence of any discrete aliphatic C—O features below 1200 cm^{-1} in the

spectra of brown coals and HI-treated lignin (cf. spectra of lignin and cellulose, Fig. 3) suggests that the content of alcoholic groups and aliphatic ethers is negligible in both, and that HI treatment splits all the aliphatic ether linkages, as well as eliminating alcoholic groups in lignin.

Pronounced changes occur in the 1600–1700 cm^{-1} region of the spectra on methylation of Victorian brown coals (Brooks, Durie, and Sternhell 1958*a*). Comparable changes were observed on methylation of the HI-treated oxidized lignin but not on methylation of HI-treated lignin.

Brooks, Durie, and Sternhell (1958*a*) discussed the effect of methylation on the spectra of brown coal at some length on the basis of available evidence. Explanation in terms of esterification of the carboxyl groups did not appear plausible at the time but a reinvestigation of the problem (Brooks *et al.* 1960) has shown that two simultaneous effects are operative, namely a shift with increase in intensity of the carbonyl group (1700–1720 cm^{-1}) due to esterification (cf. Bellamy 1958) and a shift (to lower frequencies) with decrease in intensity of the "1600 cm^{-1}" band due to methylation of phenolic groups. These changes were observed on methylation for both oxidized lignin and its product of HI treatment; but only the latter on methylation (cf. Section III (*a*)) of lignin and its product of HI treatment.

Thus methylation also reveals no basic structural differences between brown coal and HI-treated lignins. However, the increase in intensity of the C=O group absorption due to esterification is less pronounced for the HI-treated oxidized lignin than for brown coal. This may indicate that the structural environment (i.e. point of attachment) of the carbonyl groups differs with the mode of oxidation of the lignin.

The carboxyl groups in the brown coals studied may be due to oxidation during biochemical or geological changes; or, alternatively, they may derive from lignins richer than the present samples in carbonyl groups (cf. Kudzin and Nord 1951).

(*d*) *An Infra-Red Spectroscopic Study of the Isolation of Lignin from Wood*

The progress of the isolation of lignin from wood can be followed by comparing the infra-red spectrum of the treated wood at intermediate stages of the process with the spectra of cellulose and lignin. This is illustrated in Figure 4 for the preparation of the hydrochloric acid lignin from a Douglas fir sample.

As the removal of cellulose from wood progresses, those features which are characteristic of the lignin molecule at 1595, 1510, 1460, 1420, and 1265 cm^{-1} become more pronounced and the lignin bands at 1125 and 1030 cm^{-1} begin to appear as the very strong cellulose C—O and C—C absorption disappears between 1200 and 900 cm^{-1}—in particular, the characteristic cellulose bands at 1160 and 1060 cm^{-1} (Tsuboi 1957).

It seems possible that the bands due to aromatic ring vibrations in the spectrum of wood at 1590 and 1510 cm^{-1}, which are unambiguously associated with the lignin, would be of use for the quantitative determination of lignin in wood or paper pulps. The 1510 cm^{-1} band seems to be particularly suited to

this purpose since it is virtually free from interference, whereas the 1595 cm^{-1} band in wood shows some interference from the broad cellulose band near

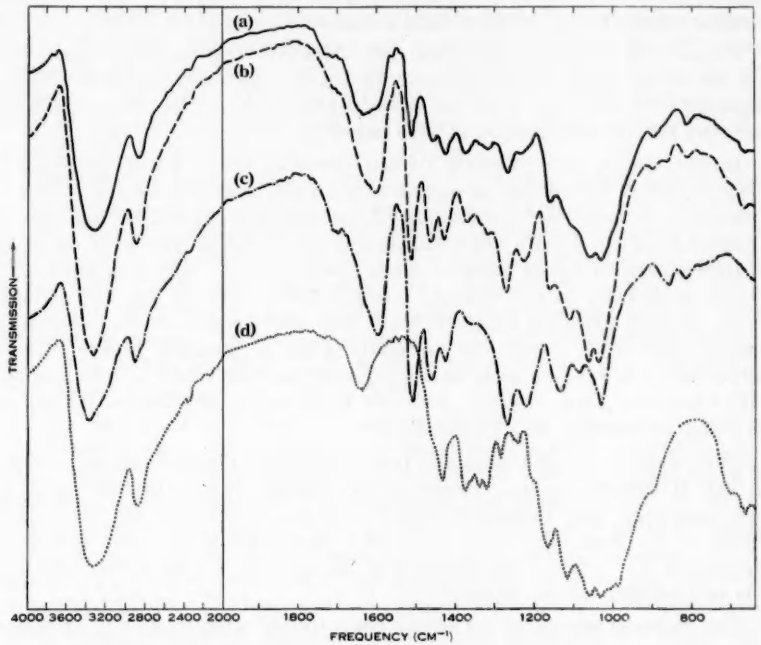

Fig. 4.—Comparison of the infra-red spectra of (*a*) wood (Douglas fir); (*b*) wood with cellulose partially removed; (*c*) lignin I (from Douglas fir); and (*d*) cellulose.

1640 cm^{-1}. If the methoxyl concentration is taken as an approximate measure of the lignin content (cf. Brauns 1952, p. 169) it can be seen from Table 3 that

TABLE 3

VARIATION OF THE INTENSITY OF THE "1600 cm^{-1}" BAND WITH METHOXYL CONTENT DURING THE ISOLATION OF LIGNIN FROM WOOD

Sample	Methoxyl (%)	Optical Density*	
		1595 cm^{-1}	1510 cm^{-1}
Wood	4·3	0·071	0·095
Partially isolated lignin	8·6	0·159	0·243
Lignin	14·3	0·203	0·287

* 1 per cent. 100 mg KCl disk basis.

there is a rough correspondence between this methoxyl content and the base-line optical densities of the 1595 and the 1510 cm^{-1} bands.

Kratzl (1956) has already suggested that quantitative studies of these bands may help clarify the question of how much aromatic fraction is present in native lignin.

The nature of the linkage of lignin in plants is still obscure and it is possible that a detailed study of many wood, lignin, and cellulose spectra, particularly in the C—O region between 1200 and 900 cm^{-1}, may throw some light on this problem. Thus, in the spectra presented here, a band which is present at 1110 cm^{-1} in the spectrum of cellulose and absent in the spectra of lignin and wood is evident in the spectrum of the partially isolated lignin. That part of the cellulose structure which is responsible for this band may be involved in chemical bonding with lignin and thus the 1110 cm^{-1} band loses its identity (as does the lignin band at 1125 cm^{-1}). On the basis of the probable assignment of this 1125 cm^{-1} band to tertiary or secondary alcohol groups (Section III (*a*) (iii)) this indicates that the chemical linkage with cellulose may occur at such a group in lignin. This is consistent with the recent work of Freudenberg (1959) from which he concludes that the carbohydrate may be attached to the cell wall (lignin) at the α-carbon atom in the phenyl propane unit.

The spectrum in the 1175 to 1000 cm^{-1} region of the partially isolated lignin resembles more closely the spectrum of cellulose than that of lignin ; for whereas the cellulose band at 1110 cm^{-1} appears yet there is no sign of the lignin 1125 cm^{-1} band.

With particular reference to the spectrum of cellulose, it is of interest to note that those features at 1160 cm^{-1} (and 1110 cm^{-1}) which it has been stated are characteristic of the cellulose ring in all cellulose derivatives (Rowen, Hunt, and Plyler 1947) are reduced in intensity on drying the cellulose.

IV. Acknowledgments

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SHORT COMMUNICATIONS

THE SPECTROPHOTOMETRIC ESTIMATION OF MOLECULAR WEIGHTS OF POLYETHYLENE GLYCOLS DISSOLVED IN BENZENE*

By R. J. W. Le Fèvre,† Gwenda M. Parkins,† and R. Roper†

In the course of other work the near infra-red spectra of six polyethylene glycols (PEG's) have been examined in benzene solution. The samples were gifts from the Shell Company and were used without further purification. "PEG's 200 and 300" were viscous oils, "800" and "1500" were waxes, while

Table 1

SPECIFIC EXTINCTION COEFFICIENTS AT 7140 cm^{-1} FOR THE POLYETHYLENE GLYCOLS DISSOLVED IN BENZENE

Solute "PEG"	c (g/100 c.c.)	I	(Log $(1/T)/cl$) $\times 10^{-2}$
200	1·6024	0·585	2·88
300	2·3700	0·515	2·43
800	2·5736	0·638	1·52
1500	2·2080	0·782	1·14
4000	1·8764	0·840	0·76
6000	1·9286	0·870	0·63

Table 2

COMPARISON OF MOLECULAR WEIGHTS FOUND CHEMICALLY OR SPECTROPHOTOMETRICALLY

Solute "PEG"	M_{chem}	M_{sp}
200	190– 200	170± 10
300	285– 315	285± 15
800	760– 840	810± 40
1500	1430–1570	1530± 75
4000	3300–3600	3760±190
6000	6000–7500	5800±290

"4000" and "6000" were apparently crystalline solids. Their molecular weight distributions, determined by end-group analyses, were as listed in Table 2 (second column). For purposes of calculation the mid-points of these ranges have been taken as the molecular weights M of the respective polymers.

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The spectra were recorded, through the 6200–8300 cm^{-1} overtone region, on a Perkin-Elmer Spectracord, concentrations of the order 2 g/100 c.c. being used in a 5-cm cell.

Each solution showed a sharp strong absorption at 7140 cm^{-1}, which being unchanged by dilution, was attributed to intramolecular hydrogen bonding (cf. Badger 1957). Other characteristics of interest found in the spectra were broad weak bands at 6400–6800 cm^{-1} (possibly caused by polymeric associations of

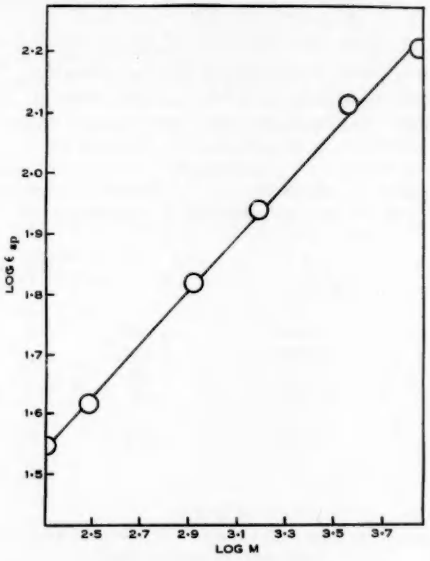

Fig. 1.—Log ε_{sp} *versus* log M.

the solute species), weak shoulders at 7040 cm^{-1}, and slight inflections at 7300 cm^{-1} (probably due to intermolecular hydrogen bonding and free-hydroxyl groups respectively (cf. Wulf and Liddel 1933, 1935, 1936; Mecke 1950; Holman and Edmondson 1956).

Quantitatively the transmission T at 7140 cm^{-1} can be related to the molecular weight of the solute. If specific extinction coefficients ε_{sp} be computed as log $(1/T) \div$ (concentration as g per 100 c.c.) $\times$ (cell length in cm), values such as those in Table 1 emerge. Log ε_{sp} is seen to have a rectilinear dependence upon log M (cf. Fig. 1); this may be expressed by

$$-\log \varepsilon_{sp} = 0 \cdot 45 \log M + 0 \cdot 51,$$

or

$$\log M = -0 \cdot 113 - 2 \cdot 22 \log \varepsilon_{sp}.$$

Table 2 illustrates the applicability of these equations to the substances under study. Agreement is satisfactory within the limits quoted, which are

based upon a 5 per cent. error in the extinction coefficient. No correction factors were applied to the measured transmissions; this was deliberate since the objective was to test a simple routine method for the determination of M. Even so, the technique is quicker and easier than the fairly involved chemical end-group analysis in current use (cf. Curme and Johnson 1952).

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SECOND VIRIAL COEFFICIENTS FOR THE STOCKMAYER POTENTIAL*

By J. A. Barker† and F. Smith†

Second virial coefficients of polar gases are often discussed in terms of the Stockmayer potential (Stockmayer 1941; Rowlinson 1949) which includes a spherically symmetrical interaction following the Lennard-Jones 12–6 law together with the electrostatic potential energy of two point dipoles:

$$u(r, \theta_1, \theta_2, \varphi_2-\varphi_1) = 4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6]-(\mu^2/r^3)[2\cos\theta_1\cos\theta_2-\sin\theta_1\sin\theta_2\cos(\varphi_2-\varphi_1)]. \quad \ldots\ldots\ldots\ldots (1)$$

Here r is the distance between the molecules and θ_1, θ_2, φ_1, φ_2 are angles specifying the orientations of the dipoles relative to the line joining them as polar axis. For this potential the second virial coefficient is given by

$$B=b_0B^*, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$-B^*=\tfrac{1}{4}\left(\frac{4}{\tau}\right)^{\frac{1}{4}}\sum_{n=0}^{\infty}\frac{2^n}{n!}\sum_{k=0}^{k\leq\frac{1}{2}n}\frac{\binom{n}{2k}\Gamma[\frac{1}{4}(2n-2k-1)]G_k t^{2k}}{\tau^{\frac{1}{4}(n+k)}}, \quad \ldots\ldots (3)$$

where $\tau=T/\theta$, $\theta=\varepsilon/k$, $t=\mu^2/\varepsilon\sigma^3\sqrt{8}$, $b_0=\frac{2}{3}\pi N\sigma^3$ and

$$G_k=\frac{1}{2k+1}\sum_{m=0}^{k}\frac{\binom{k}{m}3^m}{2m+1}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

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† Division of Physical Chemistry, C.S.I.R.O. Chemical Research Laboratories, Melbourne.

TABLE 1

VALUES OF $10^{2k} G_k/(2k)!$

k ..	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$10^{2k}G_k/(2k)!$ ..	1·00000	33·3333	400·000	2630·38	11085·9	32483·1	69819·1	114558	148023	154424	132749	95638	58569	30862	14139

TABLE 2

VALUES OF $-B^*$

t \ τ	0·7	0·8	0·9	1·0	1·2	1·4	1·6	1·8	2·0	2·5	3·0
1·6	800·2	247·0	.. 105·0	55·26	22·53	12·30	7·844	5·482	4·058	2·210	1·336
1·8	2743	673·9	240·5	110·7	37·74	18·57	11·13	7·484	5·405	2·860	1·724
2·0		2020	600·9	239·3	66·70	29·01	16·12	10·34	7·236	3·683	2·198
2·2			1623	556·9	124·8	47·17	23·97	14·50	9·771	4·733	2·776
2·4				1385	247·2	80·07	36·71	20·75	13·36	6·086	3·485

Tabulations of the function B^* are available for values of t up to 1·5 (Hirschfelder, Curtiss, and Bird 1953, p. 1147). It is sometimes desirable to use values of t greater than this, but calculation from (3) becomes very tedious under these circumstances. The purpose of this note is to transform (3) to a form which is more convenient for larger values of t and to give a short table of B^* for t up to 2·4.

By changing the order of summation equation (3) can be expressed in the form

$$-B^* = \sum_{k=0}^{\infty} \frac{H_k G_k}{(2k)!} \left(\frac{4t^2}{\tau^{3/2}}\right)^k, \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where

$$H_k(\tau) = \tfrac{1}{4}\left(\frac{4}{\tau}\right)^k \sum_{n=0}^{\infty} \frac{\Gamma[\frac{1}{4}(2n+2k-1)]}{n!} \left(\frac{2}{\sqrt{\tau}}\right)^n. \qquad \ldots\ldots\ldots \quad (6)$$

The functions H_k can be calculated from the recurrence relations

$$H_{k+2} = \frac{1}{\sqrt{\tau}} H_{k+1} + \tfrac{1}{4}(2k-1) H_k. \qquad \ldots\ldots\ldots\ldots\ldots \quad (7)$$

These relations are connected with the properties of the confluent hypergeometric function, but they can be verified directly from the definition (6). Also H_0 and H_1 can be found from the second virial coefficient for the 12–6 potential and its temperature derivative which are extensively tabulated. In fact we find

$$H_0 = -(B^*)_{12-6}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

$$H_1 = \tau^{\frac{1}{2}}[\tfrac{1}{4}(B^*)_{12-6} + (B^*_1)_{12-6}], \qquad \ldots\ldots\ldots\ldots \quad (9)$$

where the quantities $(B^*)_{12-6}$ and $(B^*_1)_{12-6}$ are tabulated by Hirschfelder, Curtiss, and Bird (1953, pp. 1114 *et seq.*; the quantity here called τ is there called T^*). Using these results B^* can be calculated for large t with much less labour than direct use of (3) would involve. For large k evaluation of G_k using (4) becomes tedious; for $k \geqslant 10$ it is sufficiently accurate to use the asymptotic formula

$$\log_{10}(G_k/(2k)!) = 0{\cdot}293406 + 1{\cdot}470649k - \log_{10} k - \left(2k + \frac{3}{2}\right) \log_{10}(2k+2)$$
$$- 0{\cdot}16286/k + 0{\cdot}13873/k^2 + 0(1/k^3). \qquad \ldots\ldots\ldots \quad (10)$$

This can be derived by standard methods from the form

$$(2k+1)G_k = \int_0^1 (1+3u^2)^k \mathrm{d}u. \qquad \ldots\ldots\ldots\ldots\ldots \quad (11)$$

Values of $10^{2k} G_k/(2k)!$ for k up to 14 are given in Table 1.

Values of $-B^*$ for t up to 2·4 are given in Table 2. This table should be used in conjunction with that of Hirschfelder, Curtiss, and Bird (1953), which gives values for t up to 1·5. The most convenient way of using these results is to prepare large-scale plots of $\log |B^*|$ against $\log \tau$; if then experimental

TABLE 3
CONSTANTS FOR ACETONITRILE

t	b_0 (cm³/mole)	θ (°K)	μ (D)	t	b_0 (cm³/mole)	θ (°K)	μ (D)
1·4	78·7	358	3·49	2·0	95·1	247	3·81
1·6	84·3	313	3·61	2·2	106	219	3·98
1·8	89·1	277	3·71	2·4	112	199	4·07

plots of log $|B|$ against log T are made on transparent paper they may be superposed on the log $|B^*|$/log τ plot and moved either vertically or horizontally to find the best fit for a given t. The values of log b_0 and log θ can then be read directly. It is usually possible to find a good fit for a range of values of t, so that t can be chosen to give a value for the dipole moment μ close to its experimental value. The dipole moment is given by

$$\mu = 0{\cdot}01759\sqrt{(b_0 t\theta)}, \quad \ldots\ldots\ldots\ldots\ldots \quad (12)$$

with μ in debye units, b_0 in cm³/mole, and θ in °K.

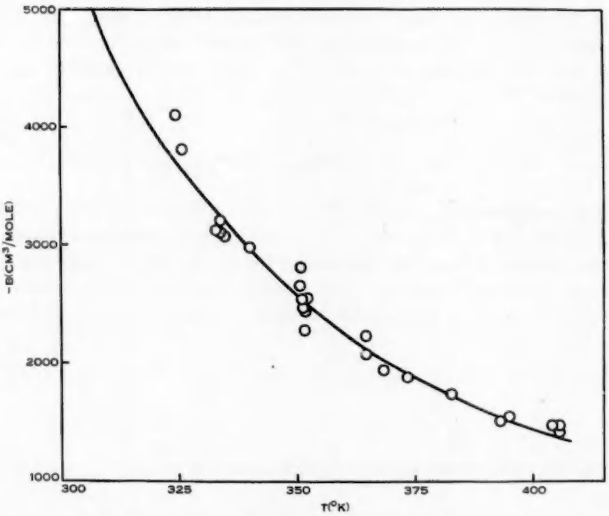

Fig. 1.—Calculated and experimental second virial coefficients for acetonitrile. Circles experimental; solid line calculated for $t=2{\cdot}2$, $b_0=106$ cm³/mole. $\theta=219$ °K.

Table 3 shows constants determined in this way for acetonitrile from the data of Lambert, Roberts, Rowlinson, and Wilkinson (see Rowlinson 1949; the individual numerical results are given in tables prepared by McGlashan 1955). The second virial coefficients are fitted equally well by any of the sets of constants

shown in Table 3. The set with $t=2\cdot2$ gives the dipole moment closest to its experimental value (the values 3·84, 3·96, and 3·97 debye are given in the literature; see Maryott and Buckley 1953). Figure 1 shows a comparison of the experimental virial coefficients with those calculated using these values of the constants. Constants found in this way can be used for interpolation and extrapolation of virial coefficient data and with appropriate combining rules for estimating virial coefficients of mixtures containing polar gases (cf. Hirschfelder, Curtiss, and Bird 1953, p. 222).

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THERMODYNAMIC FUNCTIONS OF FORMALDEHYDE*

By L. O. Dworjanyn†

Thermodynamic properties of ideal gaseous formaldehyde have been calculated from recent accurate infra-red and microwave spectroscopic data. The results obtained differ considerably from the latest published thermodynamic data.

The thermodynamic functions of formaldehyde have been previously calculated by Stevenson and Beach (1938) and by Thompson (1941). The calculations of Stevenson and Beach are based on old physical constants and on inaccurate molecular data so that the resultant functions are considerably different from the true functions. Thompson has used more recent molecular data but his results are somewhat inconsistent, particularly at high temperatures.

Recently accurately determined fundamental frequencies and moments of inertia of the formaldehyde molecule make it worthwhile to recalculate the thermodynamic functions of formaldehyde.

Calculations

The fundamental frequencies used are given by Herzberg (1945) and these are 1167, 1280, 1503, 1744, 2780, and 2874 cm^{-1}. The moments of inertia have been determined from accurate microwave spectra of formaldehyde (Lawrence and Strandberg 1951; Erlandsson 1956). The three moments are 2·974, 21·603, and $24\cdot668\times10^{-40}$ g cm^2.

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Assuming harmonic vibrations, no rotational distortion, and no rotation-vibration coupling the standard equations of statistical mechanics can be used. When the necessary data become available to correct for above assumptions the corrections can be expressed in the form of $1/T$, $\log T$, and power series of T, and added to the calculated functions (Kassel 1936).

For consistency with existing thermodynamic functions of compounds the fundamental constants from Rossini *et al.* (1952) have been used, and the principal constant R was taken as 1·98719 cal/deg mole. The resultant equation for the translational and rotational contributions to the free energy function was

$$\left(\frac{F^0-H_0^0}{T}\right)_{tr}+\left(\frac{F^0-H_0^0}{T}\right)_{rot}=-257\cdot381-4R\log T-\frac{3}{2}R\log M$$
$$-\tfrac{1}{2}R\log(I_1I_2I_3)+R\log s,$$

where F^0 is the free energy of the ideal gaseous molecule, H_0^0 is the value of the free energy at 0 °K, T is the absolute temperature, M the molecular weight, I_1, I_2, and I_3 the principal moments of inertia, and s the symmetry number. The related equations can be found in standard textbooks (Herzberg 1945) or reviews (Wilson 1940). The calculations have been carried out from first principles using a calculating machine, and these have been checked using tables of Einstein functions (Sherman and Ewell 1942).

Table 1

THERMODYNAMIC FUNCTIONS OF FORMALDEHYDE IN IDEAL GASEOUS STATE

T (°K)	$H^0-H_0^0$ (cal/mole)	$(H_0^0-F^0)/T$ (cal/mole °K)	S^0 (cal/mole °K)	C_p^0 (cal/mole °K)
298·16	2393·8	44·227	52·256	8·441
300	2410·0	44·277	52·309	8·458
400	3296·9	46·613	54·855	9·349
500	4284·9	48·485	57·055	10·418
600	5380·2	50·082	59·049	11·479
700	6578·0	51·497	60·894	12·459
800	7868·5	52·780	62·616	13·336
900	9241·5	53·964	64·232	14·106
1000	10686·4	55·067	65·753	14·776
1100	12193·6	56·105	67·190	15·355
1200	13754·8	57·086	68·548	15·855

Results

The calculated results are given in Table 1. The results are given to five significant figures although the accuracy does not in general warrant more than four figures. The extra figure will be useful for interpolation and calculation of differences, and will allow the addition of anharmonicity and other correction terms without recalculation of the functions.

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GENERAL THEORY OF ALTERNATING CURRENT POLAROGRAPHY FOR ELECTRODE REACTIONS PRECEDED BY SLOW CHEMICAL REACTIONS*

By S. SATYANARAYANA,† A. K. N. REDDY,† and K. S. G. DOSS†

There are many electrode processes in which the electrochemical reaction is coupled with a slow chemical reaction. Such electrode processes constitute an important subject for study.

The theoretical treatment of the kinetics of electrode processes has been based essentially on one of two different standpoints. Gerischer (1951, 1952, 1953*a*, 1953*b*, 1953*c*) and others have argued from considerations of an equivalent circuit. These authors have treated electrode processes with different types of rate-determining steps, and have derived expressions for the equivalent circuit elements.

A second approach is that of Breyer and Hacobian (1954). The latter have based their treatment on the direct measurement of the alternating current. They have presented clear theoretical arguments to show that both the measurement of alternating currents and the interpretation of alternating current against direct voltage curves is simpler and less ambiguous than the impedance measurements and their interpretation in the equivalent circuit method. Breyer, Bauer, and Hacobian (1955), however, have only considered electrode processes with a single rate-determining step.

In the present work, general expressions are developed for the magnitude and the phase of the alternating polarographic current resulting from electrode reactions preceded by a first-order kinetic reaction in solution.

The general reaction considered is:

$$Y \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O \overset{K_{s,h}}{\rightleftharpoons} R,$$

where the oxidant O is generated by a slow chemical reaction (with rate constants k_1 and k_2) from the substance Y. The reductant R results from the electrode reaction which is characterized by a single, heterogeneous rate constant $K_{s,h}$ following Delahay (1954). The differential equations for the system are set up by applying Fick's laws of diffusion. General solutions for the concentrations of

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oxidant and reductant are then obtained by using the Laplace transformation, and by introducing the appropriate initial and boundary conditions. Finally, the theory of absolute reaction rates is used to obtain general equations for the alternating polarographic current, and for the phase angle introduced by the kinetic reaction.

A ripple voltage superimposed upon a constant voltage is applied across the polarographic cell. As a result, there flows through the cell a current

$$i = i_0 + I \sin \omega t,$$

where i, the instantaneous current flowing through the cell, consists of a direct component i_0 (due to the applied D.C. cathodic polarization) and an alternating component $I \sin \omega t$, the alternating component of the applied voltage is then given by

$$v = V \sin (\omega t + \varphi),$$

where V is the amplitude of the applied ripple and φ is the phase angle between the applied alternating voltage and the resulting alternating polarographic current.

The phase angle φ is then related to the rate constants by equation (**1**), and the value of the alternating polarographic current I_{peak} at the summit potential E_s, that is, the peak current amplitude, is given by equation (**2**). In the equations D is the diffusion coefficient assumed to be the same for all the species, t is the time of electrolysis, and ω is the angular frequency of the applied ripple voltage.

$$\tan \varphi = \frac{-(r_1/a + r_4)}{D/K_{s,h} + r_2/a + r_5} \qquad \text{..... (1)}$$

$$I_{peak} = \frac{\left\{\dfrac{n^2F^2ADC_0^0}{RT}\right\}\alpha - \dfrac{1}{Q}[A]}{\left(\dfrac{r_1}{a}+r_4\right)\dfrac{1}{V\sin\varphi} + \dfrac{nF}{RT}\left\{\dfrac{\alpha r_3}{a} - (1-\alpha)r_6 - \dfrac{1}{Q}[A]\left[\dfrac{r_3}{a} + r_6 + \dfrac{V\sin\varphi}{2}(B) - \dfrac{V\cos\varphi}{2}(C)\right]\right\}}, \qquad \text{..... (2)}$$

where

$$a = k_1 + k_2,$$
$$r^2 = a^2 + \omega^2,$$
$$A = \frac{\alpha g_1}{a} - (1-\alpha)g_2,$$
$$B = \frac{\alpha r_1}{a} - (1-\alpha)r_4,$$
$$C = \frac{\alpha r_2}{a} - (1-\alpha)r_5,$$
$$Q = \frac{D}{K_{s,h}} + \frac{g_1}{a} + g_2,$$
$$g_1 = 2k_1\sqrt{\left(\frac{Dt}{\pi}\right)} + k_2\sqrt{\left(\frac{D}{a}\right)}\ \mathrm{erf}\ \sqrt{(at)},$$
$$g_2 = 2\sqrt{\left(\frac{Dt}{\pi}\right)},$$

$$r_1 = k_1\sqrt{\left(\frac{D}{2\omega}\right)} + k_2\sqrt{\left[\frac{D}{2}\left(\frac{r-a}{r^2}\right)\right]},$$
$$r_2 = k_1\sqrt{\left(\frac{D}{2\omega}\right)} + k_2\sqrt{\left[\frac{D}{2}\left(\frac{r+a}{r^2}\right)\right]},$$
$$r_3 = \frac{k_1}{\omega}\sqrt{\left(\frac{D}{\pi t}\right)} + k_2\sqrt{\left(\frac{D}{\pi t}\right)}\left\{\frac{\omega(1-at)}{r^2}\right\},$$
$$r_4 = r_5 = \sqrt{\left(\frac{D}{2\omega}\right)},$$
$$r_6 = \frac{1}{\omega}\sqrt{\left(\frac{D}{\pi t}\right)}.$$

In the above general theory, when it is assumed that the electrode process consists of a single rate-determining step, the equations for the alternating polarographic current which have been developed by Delahay *et al.* and also by Breyer and co-workers, can be obtained as special cases. This result is obtained, firstly, by making the rate constants for the kinetic reaction very large ($k_1=k_2\rightarrow\infty$), and secondly by setting $\alpha=0\cdot5$. These approximations also make the phase angle φ equal to 45°. The latter result for reversible reactions is the same as that obtained by earlier workers.

The details of the derivation will shortly be presented elsewhere. Work is also in progress to apply the theory to particular reaction systems.

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INFRA-RED SPECTRAL CHANGES ACCOMPANYING METHYLATION OF BROWN COALS*

By J. D. Brooks,† R. A. Durie,† B. M. Lynch,‡ and S. Sternhell†

Brooks, Durie, and Sternhell (1958) noted that methylation of Victorian brown coals by methyl iodide and sodium ethoxide in ethanol caused marked changes in their infra-red spectra in the 1600–1700 cm^{-1} region. The carbonyl band at 1700 cm^{-1} shifted to 1720 cm^{-1} with an increase in intensity; simultaneously, the band near 1600 cm^{-1} shifted from 1615 to 1600 cm^{-1} with a decrease in intensity. Somewhat similar effects were noted when humic acids were methylated (Čeh and Hadži 1956). In both papers, esterification was not regarded as the cause of the changes in the carbonyl band, since (i) available evidence suggested that the absorption coefficients of the carbonyl groups of carboxylic acids and their corresponding esters were comparable (Čeh and Hadži 1956; Brooks, Durie, and Sternhell 1958), and (ii) similar changes were not observed after brown coals had been esterified via the acid chloride (Brooks,

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Durie, and Sternhell 1958). The changes in the 1600 and 1700 cm^{-1} regions were thought to be inter-related, and it was suggested that hydrogen-bonded carbonyl groups were contributing to the 1600 cm^{-1} absorption, and that methylation shifts the freed carbonyl group absorption to 1720 cm^{-1}, where it overlaps with the carboxylic carbonyl absorption at 1700 cm^{-1}. Čeh and Hadži (1956) therefore suggested the presence of hydroxyquinones in their humic acids, but Brooks, Durie, and Sternhell (1958) considered that the magnitude of the apparent shift in carbonyl frequency was too great to be accounted for by this postulate, and they suggested that conjugatively-chelated carbonyl groups, such as occur in certain keto-enol systems, might be responsible for the changes observed on methylation of brown coal (and humic acids).

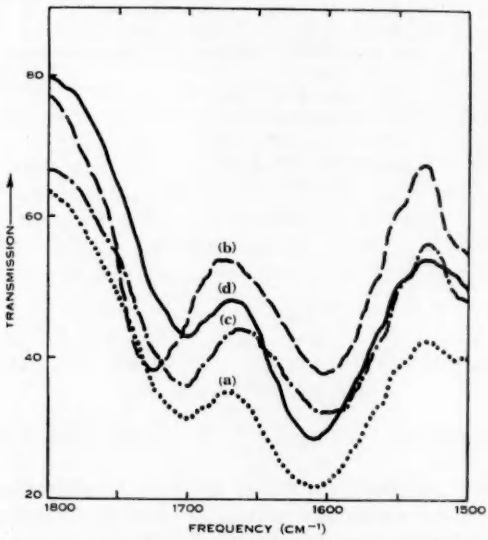

Fig. 1.—Absorption in the 1600–1700 cm^{-1} region of (*a*) Morwell brown coal (acid washed); (*b*) sample (*a*) after methylation; (*c*) sample (*b*) after saponification; (*d*) sample (*c*) after demethylation.

A more detailed study of the effects of methylation on the infra-red spectra has now been made for brown coal, lignin, and some of their chemical modification products. Diazomethane in ether-methanol was chosen as the methylating agent. The absorption maxima and base-line optical densities of the bands in the 1700 and 1600 cm^{-1} regions are listed for the various samples in Table 1, together with the carboxylic acidity where relevant.

The results obtained with Morwell brown coal (cf. Table 1 and Fig. 1) agree with those noted previously (Brooks, Durie, and Sternhell 1958), but it now appears that the spectral changes observed are the consequences of simple

methylation of carboxylic and phenolic groups.* Thus, methylation of the coal altered the intensities and positions of the bands in the 1700 and 1600 cm^{-1} regions as noted above, but alkaline hydrolysis of the methylated coal effected a reversal of the changes in the 1700 cm^{-1} region without further altering the modified 1600 cm^{-1} absorption. Furthermore, demethylation of the saponified methylated coal with hydriodic acid reversed the changes in the 1600 cm^{-1} region associated with methylation.

The independently reversible nature of the changes in these bands suggest that the change from 1700 to 1720 cm^{-1} on methylation is a consequence of the esterification of a carboxyl group (cf. Bellamy 1958), while the changes in the 1600 cm^{-1} region (decreased intensity, and a shift from 1615 to 1600 cm^{-1}) result from the methylation of phenolic groups.

Association of these changes in the 1600 cm^{-1} region with the methylation of phenolic groups is confirmed by the behaviour on methylation of a lignin with a very low carboxylic-group content, when the band near 1600 cm^{-1} changes from 1605 to 1590 cm^{-1} (cf. Table 1, and Durie, Lynch, and Sternhell 1960). Similar changes are noted when comparing the absorption bands of methoxyphenols and dimethoxybenzenes in the 1600 cm^{-1} region (*m*-methoxyphenol, $\nu_{max.}$ 1605 cm^{-1}; *m*-dimethoxybenzene, $\nu_{max.}$ 1597 cm^{-1}; *p*-methoxyphenol, $\nu_{max.}$ 1607 cm^{-1}; *p*-dimethoxybenzene, $\nu_{max.}$ 1600 cm^{-1} (Katritzky and Simmons 1959*a*, 1959*b*).

The effects accompanying methylation, subsequent saponification, and hydriodic-acid demethylation of the following materials were similar to those noted with brown coal: Morwell brown coal "hydrolysed" with aqueous potassium hydroxide at 200 °C, Klason lignin "hydrolysed" with ethanolic potassium hydroxide at 200 °C or oxidized with oxygen in alkali (cf. Table 1). However, with a brown coal sample "hydrolysed" with ethanolic potassium hydroxide at 200 °C, the optical density of the carbonyl band decreased on methylation. With some brown-coal derivatives which had been oxidized quite extensively in alkali, the optical densities in both the 1700 and 1600 cm^{-1} regions decreased on methylation, and the changes in the 1600 cm^{-1} region were accompanied by shifts to higher frequencies (cf. Table 1). These deviations from the "normal" behaviour probably reflect variations in the environment of the absorbing centres, but the changes induced are still reversed on saponification followed by demethylation.

The consistent decrease in the optical density of the "1600 cm^{-1}" band on methylation is due mainly to weight-factor changes (cf. Durie and Sternhell 1959).

Although further work on the significance of the intensity changes in the 1600–1700 cm^{-1} region is obviously desirable, it can be concluded that these

* The earlier conclusion concerning esterification (cf. p. 179) must be disregarded, since it has been established that it is difficult to esterify the carboxylic groups of brown coal quantitatively using the acid chloride as intermediate. It is also evident that considerable differences exist in the absorption coefficients of carbonyl groups in carboxylic acids and in the corresponding esters, i.e. "major changes in carbonyl intensity occur with change in carbonyl function" (Bellamy 1958).

TABLE 1

EFFECTS OF METHYLATION ON THE 1600–1700 cm^{-1} BANDS IN BROWN COAL, LIGNIN, AND THEIR DERIVATIVES

Sample	Carboxyl-Carbonyl Band		Carboxylic Acidity (m-equiv/g; dry basis)	"1600 cm^{-1}" Band	
	$\nu_{max.}$ (cm^{-1})	Optical Density*		$\nu_{max.}$ (cm^{-1})	Optical Density*
I. (*a*): Morwell brown coal (acid-washed) ..	1700	0·143	1·78	1615	0·377
(*b*): (*a*), methylated ..	1720	0·226	—	1600	0·286
(*c*): (*b*), saponified ..	1700	0·162	—	1600	0·286
(*d*): (*c*), demethylated ..	1700	0·124	1·70	1615	0·344
II. (*a*): Morwell brown coal treated with aqueous KOH at 200 °C ..	1705	0·277	2·61	1615	0·401
(*b*): (*a*), methylated ..	1735	0·301	—	1600	0·188
(*c*): (*b*), saponified ..	1700	0·182	1·75	1600	0·188
III. (*a*): Morwell brown coal treated with ethanolic KOH at 200 °C ..	1700	0·235	1·90	1615	0·171
(*b*): (*a*), methylated ..	1735	0·176	—	1600	0·111
(*c*): (*b*), saponified ..	1705	0·218	1·20	1600	0·178
IV. (*a*): Morwell brown coal oxidized with oxygen and alkali	1705	0·365	4·32	1615	0·448
(*b*): (*a*), methylated ..	1725	0·314	—	1620	0·276
V. (*a*): Yallourn brown coal treated with aqueous KOH at 200 °C, then oxidized with oxygen and alkali	1705	0·432	4·51	1610	0·414
(*b*): (*a*), methylated ..	1730	0·333	—	1625	0·291
VI. (*a*): Klason lignin from Pacific maple	1700	0·030	0·50	1605	0·296
(*b*): (*a*), methylated ..	1720	0·047	—	1590	0·269
VII. (*a*): Klason lignin treated with ethanolic KOH at 200 °C	1700	0·055	0·90	1607	0·331
(*b*): (*a*), methylated ..	1725	0·089	—	1590	0·256
VIII. (*a*): Klason lignin oxidized with oxygen and alkali	1705	0·094	1·43	1605	0·286
(*b*): (*a*), methylated ..	1725	0·074	—	1595	0·220
(*c*): (*b*), saponified ..	1700	0·098	1·00	1595	0·300
(*d*): (*c*), demethylated ..	1705	0·076	1·62	1600	0·368
(*e*): (*d*), remethylated ..	1730	0·156	—	1595	0·279

* 1%, 100 mg KCl disk basis.

changes are not due to the presence of any unusual type of carbonyl group in the brown coals (contrast Brooks, Durie, and Sternhell 1958; Čeh and Hadži 1956), but result from changes of carboxyl groups to methoxycarbonyl groups, and phenolic groups to methoxy groups. In view of these conclusions, a more detailed examination of the changes in absorption in the 1600 and 1700 cm^{-1} regions observed after the methylation of carbon blacks (Garten, Weiss, and Willis 1957; Hallum and Drushel 1958) is indicated.

Experimental

The various samples examined were prepared as described previously (Durie and Sternhell 1958; Lynch *et al.* 1959; Durie, Lynch, and Sternhell 1960). Methylations were carried out using a large excess of diazomethane in ether-methanol (10 : 1). Several successive treatments were employed and reactions were carried out below 5 °C to minimize thermal decomposition of the diazomethane. Saponification of the ester groups in methylated samples was effected by refluxing with 2N sodium hydroxide under nitrogen. Demethylations with hydriodic acid were carried out using the conditions of the Zeisel method.

Infra-red spectroscopic measurements were carried out using a Perkin-Elmer Model 21 double-beam infra-red spectrophotometer (rock-salt prism), and employing the general techniques adopted by Brooks, Durie, and Sternhell (1958). Optical densities were measured using the base-line technique (Wright 1941), and the base-line positions chosen were those employed by Durie and Sternhell (1959).

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THE δ-HYDROXYACIDS OF WOOL GREASE*

By C. S. Barnes†

Radell, Eisner, and Donahue (1954) reported the isolation of a neutral fraction after treatment of wool grease acids with aqueous-ethanolic hydrochloric acid. This neutral material was obtained in 12 per cent. yield, and had a composition approximating to $C_{20}H_{38}O_2$. Its infra-red absorption showed absence of hydroxy groups and the carbonyl absorption was consistent with a δ- but not a γ-lactone. The cryoscopically determined molecular weight and the saponification equivalent were about equal so that a lactide structure could be excluded. No unsaponifiable material was obtained on hydrolysis, but methanolysis gave a hydroxymethyl ester. These results were interpreted to mean that the neutral fraction was a δ-lactone (or mixture of δ-lactones) derived from the corresponding acid(s) present in the grease.

This conclusion is interesting because it means that a major group of acids of unusual structure has been overlooked by other investigators (for review see Horn and Pretorius 1956; Truter 1956; Downing, Krantz, and Murray 1960). However, the evidence would also be consistent with the presence of large ring lactones formed from the ω-hydroxy acids known to be in the grease, and the infra-red absorption of the carbonyl group is that expected for a simple linear ester. The evidence for lactone formation rests on the absence of an unsaponifiable fraction after hydrolysis under unspecified conditions, and the presence of hydroxyl absorption in the infra-red absorption spectrum of the methanolysis product. The procedure of Radell, Eisner, and Donahue (1954) involved heating the wool grease acids with acidic aqueous ethanol and partial esterification might therefore be expected. At least some portion of their neutral fraction should be simple monofunctional esters. Although these could not give rise to a methanolysis product showing hydroxyl absorption, it is frequently difficult to ensure complete absence of hydroxylic solvents from amorphous systems.

For these reasons it seemed desirable to re-examine the evidence for δ-hydroxy acids in wool grease.

Esterification of Wool-Grease Acids

Using conditions similar to those of Radell, Eisner, and Donahue (1954), wool-grease acids which had been prepared by saponification of wool grease according to the method they had used, were treated with aqueous-ethanolic hydrochloric acid, and in this way gave material the acid value of which had been

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reduced by about the same extent as they had observed. The neutral fraction was obtained by incomplete neutralization followed by percolation in light petroleum over neutral alumina. Thus isolated, the neutral fraction was obtained in 13 per cent. yield and had no hydroxyl absorption, but had carbonyl absorption at 1740 cm^{-1} attributable to an ester or to a δ- or higher membered lactone. The close agreement between this fraction and Radell, Eisner, and Donahue's neutral material is seen from Table 1. Agreement extends to the elementary analysis and the saponification equivalent. The analysis, as also theirs, agrees better with $C_{22}H_{44}O_2$ rather than their preferred $C_{20}H_{38}O_2$ which presumably was selected to agree with the saponification equivalent. However, the results of methanolysis differed. The product showed no absorption in the infra-red to support the presence of hydroxyl groups. Furthermore, the acid mixture obtained from alkaline hydrolysis likewise failed to show such absorption. The possible presence of lactones, except in trace amounts, was thus excluded.

TABLE 1

Substance	Acid Value	Sap. Value	Miscellaneous
1. Wool-grease acids	156	176	I.R.* 3450, 1750, 1715 c
2. 1 treated with H_2O-EtOH-HCl in open vessel	144	173	
3. 1 treated with H_2O-EtOH-HCl under reflux	96	175	
4. Wool-grease acids treated by Radell, Eisner, and Donahue (1954)	103	167	
5. Neutral from 3	0	175 312†	C, 77·8; H, 12·9% $[\alpha]_D$ +2°, I.R. 1740
6. Neutral from 4	—	311†	C, 77·7; H, 12·8% $[\alpha]_D$ +13°, I.R. 1738

* I.R., infra-red absorption (cm^{-1}).

† Saponification equivalent.

These results can be interpreted simply on the basis of partial esterification of the wool-grease acids with ethanol, and absorption of the hydroxy esters and unesterified acids on alumina. As further evidence it was noticed that when an open vessel was used for the acid treatment, a proportion of the ethanol was lost by evaporation and the reduction in acid value was less than after corresponding treatment under a reflux condenser. Finally, a comparison of the neutral hydroxyl-free fraction from aqueous-ethanol-treated wool-grease acids gave on gas chromatography a pattern identical with that given by hydroxyl-free esters prepared by direct ethylation. Since the total ethyl esters contained 66 per cent. unhydroxylated esters, it follows that 20 per cent. of the acids were esterified under the conditions used. It must be concluded that neither δ-hydroxy acids nor δ-lactones was present.

Experimental

(*a*) *Acid Treatment of Wool-Grease Acids.*—To simulate the conditions obtained after saponification (Barnes, Curtis, and Hatt 1952), wool-grease acids (50 g) were dissolved in hot 90% ethanol (300 ml) containing sodium hydroxide (12 g). After heating for 15 min, water (600 ml) and conc. hydrochloric acid (60 ml) were added and the mixture stirred at 68±2 °C for 4 hr under reflux. The product was isolated by dilution with water, chloroform extraction, and water washing.

In a similar way the acids were treated in an open flask. Acid and saponification values are shown in Table 1.

(*b*) *Isolation of Neutral Fraction.*—A portion (10 g) of the product obtained from HCl treatment of the acids under reflux as above was dissolved in ethanol and sufficient sodium hydroxide in ethanol added to bring it to near neutrality. The unsaponified material was extracted with hexane and filtered through alumina to give after evaporation an almost colourless solid (1·3 g) containing some crystals which melted to a mobile oil at about 30–35 °C. Its analytical values are shown in Table 1. Passage at 250 °C and 500 mm over "Silicone" (10%) supported on "Celite" gave a trace showing 21 components.

(*c*) *Methanolysis of Neutral Fraction.*—The neutral fraction (300 mg) was refluxed for 6 hr in methanol (100 ml) and conc. sulphuric acid (1 drop), when it was recovered by dilution with water, extraction with ether, and drying by boiling down several times with light petroleum. The infra-red absorption spectrum as a Nujol mull had a band at 1745 cm^{-1} and no hydroxyl absorption.

(*d*) *Saponification of Neutral Fraction.*—The neutral fraction (1 g) was saponified by refluxing for 1 hr with 4% ethanolic potassium hydroxide (50 ml). The acids were recovered by ether extraction of the diluted and acidified solution, and dried by boiling down several times with light petroleum. The infra-red absorption spectrum as a Nujol mull showed a carbonyl band at 1715 cm^{-1} and no hydroxyl absorption.

(*e*) *Hydroxyl-Free Wool-Grease Acid Ethyl Esters.*—Wool-grease acids (12 g) in ethanol (99%; 400 ml) and sulphuric acid (20 ml) were refluxed for 1 hr. Only traces of acid were removed on washing with alkali, and the product was filtered through alumina in hexane to remove hydroxy esters. The yield (7·5 g) corresponded to 66% non-hydroxylated acids in the original wax. Gas chromatography in a manner identical with that described in (*b*) above gave a pattern identical with that from the neutral fraction. The infra-red absorption spectrum of a liquid film was identical with that of the neutral fraction from (*b*).

Dr. D. T. Downing is thanked for a gift of wool-grease acids, and Mr. Z. Krantz for running the gas chromatograms.

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